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EXPERIMENTAL PRODUCTION OF ROOFING FELTS

By Merle B. Shaw, George W. Bicking, and O. G. Strieter [1]

ABSTRACT

An investigation is being conducted at the bureau to determine the relative value of different fiber compositions in the life and serviceability of asphalt saturated and coated roofing felts. Experimental felts composed of varying proportions of the usual felt-making fibrous materials, and with a high content of low-grade substitutes not employed commercially in roofing felts, were made for the investigation.

The paper-making materials employed were No. 2 roofing rags, old jute and manila bagging, old newspapers, and finely ground wood sawdust. One felt contained as high as 60 per cent of wood-fiber papers and 30 per cent of sawdust. The paper-making processes consisted of beating the raw materials and converting the prepared stock into a sheet of paper, or felt. The waterleaf felts were made in the semicommercial paper mill of the bureau but were saturated and coated, and thus converted into roofing, in a commercial roofing mill.

Measurements made on the basic papers, the saturated felts, and the finished roofing and analyses of the saturant and of the coating employed are given. To permit comparison of the experimental felts with the commercial product, corresponding data are included for commercial roofing.

The results indicate that relatively large amounts of substitute materials can be used in admixture with rag stock without causing great difficulty in the manufacturing processes. The work at the bureau was on a semicommercial scale, but comparison of the data for the experimental and the commercial felts indicates that the results obtained can be applied directly to commercial practice.

If the durability tests now in progress show that the presence of the substitutes does not decrease the life of the felts in service, the use of these materials in admixture with rag stock would effect considerable economy in the production of roofing felts. The lower cost of the substitute materials and the saving in time and power required for the paper-making process would both contribute materially to reduce the manufacturing costs.

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[1] Research associate of the Manufacturing and Industrial Research Committee of the Asphalt Shingle and Roofing Institute.

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I. INTRODUCTION

The paper felts used as the base of asphalt roofing materials are made of rags, with or without the addition of substitutes. Owing to the increased cost of rags in recent years, more extensive use of substitute materials in admixture with the rag stock seems inevitable. Accordingly, an investigation to determine the relative value of different fiber compositions on the life and serviceability of roofing materials is being conducted at the Bureau of Standards. The production of the experimental felts described in this publication is a part of that investigation.

Paper felts composed of varying mixtures of the usual felt-making fibrous materials, and with a high content of low-grade substitutes, were needed for the investigation. Because of the high content of substitute materials desired, the felts could not be obtained commercially. Since considerable economy could be effected by the use of the substitutes, if the life of the felts in service would not be materially impaired thereby, it was desired to include papers containing them. The manufacture of the papers was undertaken at the bureau at the request and with the cooperation of the Manufacturing and Industrial Research Committee of the Asphalt Shingle and Roofing Institute. The papers produced were subsequently converted into asphalt roofing in a commercial roofing mill.

II. DESCRIPTION OF COMMERCIAL MANUFACTURE OF ROOFING FELTS

For the reader not familiar with the commercial manufacture of asphalt roofing felts the following brief description is given:

The paper felts are generally formed on a cylinder paper-making machine.[2] The processes of manufacture are similar to those employed in paper making in general and consist, therefore, of pulping the fibrous material and converting the prepared pulp into a dry, continuous sheet on the paper machine. The felt is impregnated with asphalt by running the sheet through a tank containing asphalt maintained at a high temperature (350 to 400° F.). The amount of saturant absorbed is dependent on the time the sheet is immersed and the absorptive quality of the felt. After leaving the tank the felt passes around steam-heated rolls which drive in the saturant and remove the excess, so that the surface is dry when the sheet leaves the machine.

The coating is applied by steam-heated coating rolls. Melted asphalt is flowed on the upper side of the sheet and spread uniformly by the upper roll. The excess quantity is allowed to flow into a small tank underneath, where it is picked up by the lower coating roll and spread on the under side of the sheet.

The coated felt while hot is passed under a hopper, where particles of talc, sand, or other granular material are sifted on the surface, and then around cold rolls which firmly press the mineral matter into the hot, soft coating. After cooling, the felt is either wound into rolls or cut into sheets as requirements demand.

Additional information on the properties of asphalt saturant and coating is included in the data on the saturating and coating of the experimental felts.

III. SEMICOMMERCIAL PAPER-MAKING TESTS

1. PAPER-MAKING MATERIALS

The paper felts must have sufficient strength not to break during the processes of saturation and coating. They must also be sufficiently porous in structure to absorb the proper quantity of the asphalt saturant. The kind and proportion of substitutes that can be employed depend, therefore, on the physical properties of the materials.

The paper-making materials used in the experimental felts were No. 2 roofing rags, old jute and manila bagging, old newspapers, and finely ground wood sawdust.

[2] The authors know of only one commercial mill using a Fourdrinier paper machine in the manufacture of roofing felt. The equipment of that mill included the Fourdrinier machine, but not a cylinder machine, before roofing felts were made there, which may account for its use.

2. EQUIPMENT

Although the paper mill of the bureau is equipped for making paper on a semicommercial scale under practical mill conditions, it does not include a cylinder, or felt-making, machine and is therefore not well adapted to making heavy papers of the roofing-felt type. The equipment employed was that in general use in the bureau mill and consisted of a 50-pound wood tub beater, with manganese-bronze bars and plate; a 300-pound tile-lined beater, with phosphor-bronze bars and plate; a small Jordan refiner, with iron bars; a 4-plate screen; and a 29-inch Fourdrinier paper-making machine, with wire 33 feet long and having two presses, nine 15-inch driers, a small machine stack of 7 rolls, and a reel.[3]

3. PROCEDURE

The rags supplied for the tests had been cut into small pieces previous to shipment. The subsequent manufacturing processes consisted, therefore, in beating the raw materials to a pulp and converting the prepared stock into a sheet of paper, or felt.

The strength of the felt depends not only on the physical properties of the raw materials, but also upon the paper-making processes controlling the length of the fibers and the formation of the sheet.

(*a*) BEATING.—The procedure followed in the beating treatment of the different furnishes was established by preliminary experimental tests in the 50-pound beater. The pulps used in the felts described herein, however, were prepared in the 300-pound beater.

Six beaters of stock were prepared. The furnishes employed were—

No. 1, 100 per cent rag.

No. 2, 60 per cent rag, 30 per cent newspaper, 10 per cent sawdust.

No. 3, 10 per cent rag, 60 per cent newspaper, 30 per cent sawdust.

No. 4, 60 per cent rag, 20 per cent bagging, 20 per cent newspaper.

No. 5, 66.7 per cent bagging, 33.3 per cent newspaper.

No. 6, 100 per cent bagging.

The beating intervals for the furnishes were 5½, 2¾, 1, 5⅙, 4¾, and 6¼ hours, respectively.

The rags and bagging for each beater were prepared first and the substitute materials were added later. Owing to the small quantity of rags in lot No. 3, the rags were prepared in the 50-pound beater and transferred to the 300-pound beater for the final beating and mixing. The beating interval given for this lot is that in the

[3] Photographs of the equipment, except the 300-pound beater, are given in B. S. Tech. Paper No. 340, Caroá Fiber as a Paper-Making Material.

larger beater. The rags and bagging of lot No. 4 were treated together.

To produce a felt of open texture with good absorptive quality respecting impregnation with asphalt, vigorous and rapid beating of the stock, with comparatively little hydration, was required. The beater roll was, therefore, lowered as rapidly as the capacity of the motor would permit. The beating progress could doubtless have been accelerated, however, without impairing the quality of the stock.

Prolonged beating causes fibers to disintegrate or split longitudinally into fine fibrillæ. The frictional action in the beating process also has a gelatinizing effect on the surface of the minute fibrous tissues and causes them to become semicolloidal in state. Such stock is said to be "hydrated," "wet," or "slow." Water drains from it slowly on the paper-machine wire, and the finely divided fibers can, therefore, be shaken into a well-felted, smooth-surfaced sheet. The sheet produced has relatively low porosity, however, and, therefore, could not absorb sufficient saturant to give the fibers the degree of protection required for roofing felt.

The rate at which water drains from the pulp is termed "freeness." Measurement of this property at progressive intervals during a beating operation shows the relative "drainability" of the stock and, therefore, serves as an indication as to the progress of the beating. Since all fibers do not hydrate at the same rate, however, the freeness readings for different furnishes do not necessarily gage their comparative fiber lengths.[4]

The fibers in the beater furnishes, previously listed, differ in physical characteristics and, therefore, in rate of hydrating. Consequently, no attempt was made to beat the pulp to a definite freeness reading in the tests described herein. In a mill running on one grade of raw material, however, freeness measurements would doubtless be an effective method of control in maintaining a uniform product.[5]

(*b*) Paper-Machine Operation.—As previously stated, the bureau paper mill is not equipped with a cylinder machine, the type usually employed commercially for roofing felts, nor is the equipment well adapted to the manufacture of thick papers. Experimental difficulties were experienced in using the small Fourdrinier machine owing to the inadequate capacity of the pump and the drying machinery. The felts made were, however, pronounced very satisfactory by experts of the roofing institute.

[4] A more detailed discussion of the theory of hydration and freeness measurements is given in B. S. Tech. Paper No. 329, Research on the Production of Currency Paper in the Bureau of Standards Experimental Paper Mill.

[5] Philip W. Codwise, The Freeness Test in Roofing-Felt Manufacture, Paper Trade J., 85, No. 4, pp. 52-54; July 28, 1927.

The prepared stock was pumped from the Jordan refiner directly to the paper machine and converted into a continuous sheet. The limited capacity of the pump necessitated reduction of the width of the sheet to 16 inches in order to obtain the weight desired. A 50-pound felt was originally planned and was made, even with the inadequate pumping facilities, but experimentation showed that a more uniform product could be obtained if the weight was decreased. Accordingly, the weight of the final test felts was reduced to from 40 to 44 pounds.

Difficulty was encountered also in drying the felts. The drying machinery of the bureau's equipment was designed for thin papers, whereas the felts were comparatively thick and held large quantities of water. To overcome the drying difficulty the felts were passed twice over the drying rolls. The moisture content of the finished sheets was about 7 per cent.

IV. MEASUREMENTS ON FINISHED WATERLEAF-PAPER FELT

The fiber composition of the beater furnish for each machine run and various measurements on the finished waterleaf or unsized sheet are given in Table 1. The apparatus and methods employed in obtaining the measurements are either described herein or are available in other publications.

TABLE 1.—*Test data on finished waterleaf felt*

Felt No.	Mill furnish	Microscopic analysis of waterleaf felt: Rag	Wool	Jute and manila	Chemical wood	Ground wood	Weight (moisture free): Per 480 square feet	Per 100 square feet	Bursting strength	Thickness	Tensile strength: Machine direction	Tensile strength: Across machine direction	Tearing strength: Machine direction	Tearing strength: Across machine direction	Ash in dry (moisture free) felt	Pliability on mandrel	Saturation: Kerosene	Saturation: Calculated asphalt	Xylol test
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Lbs.*	*Lbs.*	*Points*	*Inch*	*Lbs.*	*Lbs.*	*g*	*g*	*P. ct.*		*P. ct.*	*P. ct.*	*Sec.*
A. BUREAU OF STANDARDS PAPER																			
1	100 per cent rag	90	5	------	5	------	43.9	9.1	44	0.0428	34	25	496	384	7.09	All satisfactory on 1/16-inch mandrel.	128	164	69
2	60 per cent rag, 30 per cent newspaper, 10 per cent sawdust.	45	5	------	15	35	45.4	9.5	32	.0501	29	18	464	320	5.63	7 of 12 samples cracked on 1/16-inch mandrel.	147	189	61
3	10 per cent rag, 60 per cent newspaper, 30 per cent sawdust.	10	------	------	25	65	44.2	9.2	37	.0541	37	27	384	256	2.07	8 of 12 samples cracked on 1/8-inch mandrel.	154	198	55
4	60 per cent rag, 20 per cent bagging, 20 per cent newspaper.	55	5	15	5	20	40.0	8.3	45	.0419	38	27	512	400	5.79	8 of 12 samples cracked on 1/16-inch mandrel.	132	168	66
5	66.7 per cent bagging, 33.3 per cent newspaper.	10	------	60	10	20	40.7	8.5	43	.0453	40	31	512	368	5.56	7 of 12 samples cracked on 1/8-inch mandrel.	148	189	37
6	100 per cent bagging	15	5	80	------	------	41.4	8.6	37	.0495	33	27	512	384	6.04	9 of 12 samples cracked on 1/16-inch mandrel.	171	220	17
B. COMMERCIAL PAPER																			
2	100 per cent rag	83	4	6	5	2	49	10.2	45	0.0530	37	19	608	416	6.8	All satisfactory on 1/16-inch mandrel.	160	205	25
3	60 per cent rag, 40 per cent sulphite pulp.	47	2	6	45	------	50	10.4	52	.0534	45	21	768	544	5.3	----do----	149	191	25
10	80 per cent rag, 20 per cent newspaper.	63	9	7	7	14	54	11.2	47	.0681	35	19	752	512	6.0	----do----	189	243	16
13	80 per cent rag, 20 per cent mixed paper.	61	6	18	15	------	51	10.6	46	.0592	38	18	704	496	6.5	----do----	166	212	18
17	60 per cent rag, 40 per cent bagging.	59	7	29	5	------	51	10.6	38	.0582	34	17	688	416	6.4	----do----	171	219	28
22	80 per cent rag, 20 per cent ground-wood pulp.	42	2	28	2	26	47	9.8	42	.0591	35	18	672	464	6.0	----do----	182	234	16

Under "mill furnish" is given the percentages by weight of the raw materials furnished to the beater in the manufacture of the felts. The fiber composition of the finished waterleaf paper is shown under "microscopic analysis." The miscroscopic determinations were made by the dot-count method, of which an adaptation suitable for paper felt was developed at the bureau.[6] The seeming discrepancies in the composition determined by the laboratory analytical procedure and that given by the mill manufacturing practice can be largely accounted for by the quality of the raw materials. Roofing rags are, in general, the lowest-grade sortings from the mixed-rag collection, and the cotton rags employed (No. 2 roofing rags are classified as cotton) doubtless contained some extraneous fibers. Also sawdust is not clearly distinguishable from ground wood under the microscope and was doubtless therefore reported as ground wood by the analyst.[7] Considering these facts, the results are in good agreement.

Felt weights are given on the basis of 480 square feet. The felts are customarily spoken of as "light," "medium," or "heavy," depending on the weight. Those given in the table are considered medium. The strength tests—bursting, tensile, and tearing—and the thickness measurements were made under the standard atmospheric conditions for paper testing, 65 per cent relative humidity and 70° F. temperature, and by standard methods.[8]

Data on the pliability and the saturability also are necessary in determining the value of roofing papers and similar materials, therefore measurements of these qualities were included.

The pliability test consisted in bending 1-inch strips of the dry felt over mandrels at a uniform rate and recording the number of strips that cracked and the diameter of the cylinder on which the cracking occurred. (The pliability test for saturated felts is on moistened samples.[9]) The strips were cut lengthwise from the rolls and the the bending was through an arc of 180° in two seconds of time.

The kerosene and xylol tests were made to determine the saturating quality of the felts. The methods used were those recommended by the Prepared Roofing Association some years ago.[10]

The object of the kerosene test was to obtain a figure for the maximum saturating capacity of the felts. A sample of the dry felt was saturated with a measured volume of kerosene in order to determine

[6] R. E. Lofton, Determination of the Fiber Composition of Roofing Felts, Paper Trade J., 84, No. 14, pp. 57-58; Apr. 7, 1927.

[7] See footnote 6.

[8] These measurements and the ash determination were made by methods described in Paper Testing Methods, published by the Technical Association of the Pulp and Paper Industry, 18 East Forty-first Street, New York, N. Y. The tensile-strength measurements were made on a Scott tensile tester.

[9] Test same as that specified in United States Government Master Specification No. 295; also same as that described in Asphalt and Allied Substances, by Herbert Abraham, 2d ed., corrected, p. 560; 1920.

[10] Reports of Technical Committee of the Prepared Roofing Association; 1923.

the amount of voids. From the results obtained the theoretical maximum per cent of asphalt saturation of the sheet was computed. The computation involved the weight of the sample, the volume of kerosene the sample absorbed, and the specific gravity of asphalt, which was assumed to be 1.05. In Table 1 the maximum saturating capacity is reported in two ways, namely, under the first caption as the saturation capacity expressed in terms of kerosene, and under the second caption as calculated asphalt.[11]

The xylol test supplements the kerosene test and has for its purpose the ascertainment of the speed with which saturation takes place. The test consisted in timing the rate of rise of the xylol by capillarity in a strip of the felt, one end of which was immersed in the xylol. Test strips 15 mm wide and of suitable length were cut lengthwise from the sheet, and pencil lines were drawn across at 1 and 4 cm from one end of each. The time required for the xylol to rise the 3 cm intervening between the marks was noted and is reported in the table as the xylol test for the sample under consideration.

V. SATURATED FELTS

1. METHOD OF SATURATING PAPER FELTS

The felts were saturated by a roofing manufacturer using a regular large-scale production roofing machine. The objective was to keep the saturation around 140 per cent, based on the weight of the felt. To permit comparison of the test specimens, uniformity of saturation and equal amounts of saturant in all the felts were required. Specifications for asphalt roofing require, in general, that the minimum percentage of saturant be 130 for medium-weight felts and 140 for heavy, hence 140 was arbitrarily chosen for the experimental tests.

Because of the different physical characteristics of the substitutes used, the felts differed considerably in saturating capacities. To keep the saturation of the more porous ones down to the percentage specified was, of course, very difficult and, as Table 3 shows, was not always achieved.

2. ANALYSIS OF SATURANT USED

The analysis of the asphalt saturant used (for both bureau and commercial felts) is given in Table 2. Most of the tests have been adopted as standard by technical societies, particularly the American Society for Testing Materials and the Prepared Roofing Association, and are described in detail in the publications of those organizations. The methods are also outlined in United States Government Master Specification No. 84.

[11] Test is fully described in The Kerosene Test for Roofing Felt, by P. W. Codwise, Paper Trade J., 87, No. 12, p. 60; Sept. 20, 1928.

TABLE 2.—*Analysis of asphalt saturant and coating*

	Specific gravity at 77/77° F.	Melting point (ring-and-ball method)	Ductility at 77° F. (5 cm per minute)	Loss on heating 5 hours at 325° F.	Matter insoluble in cold CS_2	Ash	Penetration, in 0.01 cm units			
							200 g, 60 seconds at 32° F.	100 g, 5 seconds at 77° F. before heating	100 g, 5 seconds at 77° F. after heating	50 g, 5 seconds at 115° F.
		° C.	*cm*	*Per cent*	*Per cent*	*Per cent*				
Saturant for bureau felt	1.001	45.3	48.3	0.07	0.50	0.10	64.0	143.0	116.0	(1)
Saturant for commercial felt	1.035	45.9	(1)	.18	.20	.23	35.4	121.0	112.0	(1)
Coating for bureau felt	1.020	97.3	4.3	.02	.45	.10	11.0	16.0	14.0	37.0
Coating for commercial felt	1.034	100.9	4.15	.16	.70	.48	14.9	19.7	19.4	40.6

[1] Not determined. Too soft. [2] Over 100.

The specific-gravity test is of value for controlling uniformity of supply and for figuring the weight of a given volume. The hydrometer method is generally used to measure the specific gravity, and the standard temperature at which the determination is made is 77° F. for bituminous materials.

The melting point was determined by the ring-and-ball method, which is essentially as follows: The ring is filled with asphalt, the ball is placed on the center of the upper surface, and the completed unit is suspended at a definite depth in a glass vessel of freshly boiled distilled water at 5° C. Heat is applied to the bottom of the vessel at such a rate as to raise the temperature of the water 5° C. each minute. The temperature recorded at the instant the melted asphalt touches the bottom of the vessel is reported as the melting point.

The ductility of an asphalt is defined as the distance to which it will elongate before breaking, when the two ends of a briquet of the material are pulled apart at a specified speed and temperature. When the conditions of test are not specifically stated, the speed and the temperature are understood to be 5 cm per minute at 77° F. (25° C.).

To determine the loss on heating, a sample of the asphalt in a tared container is placed in a constant-temperature oven and maintained at 325° F. (163° C.) for five hours. After cooling, the sample is weighed and the loss due to volatilization computed.

The material that does not go into solution by cold extraction with carbon bisulphide is reported as insoluble matter.

Penetration is defined as the consistency of a bituminous material expressed as the distance that a standard needle vertically penetrates a sample of the material under known conditions of loading, time, and temperature. The combinations of these conditions given in the table are all standard.

3. MEASUREMENTS ON SATURATED FELTS

Measurements on the saturated felts are shown in Table 3. The methods of test for the saturated felts, except for water absorption, are fully described in United States Government Master Specification No. 295 and the text, Paper Testing Methods to which reference has previously been made (footnote 8).

TABLE 3.—*Test data on saturated felt*

A. BUREAU OF STANDARDS PAPER

Felt No.	Felt composition	Weight		Constituents		Saturation of felt	Loss on heating at 105° C. for five hours	Ash in desaturated felt	Moisture in felt (xylol method)	Bursting strength	Thickness		Tensile strength		Tearing strength		Pliability on mandrel at 10° C.	Water absorption (at 25° C. for 24 hours)
		Per 480 square feet	Per 100 square feet	Felt	Bitumen						Saturated felt	Desaturated felt	Machine direction	Across machine direction	Machine direction	Across machine direction		
		Lbs.	*Lbs.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Points*	*Inch*	*Inch*	*Lbs.*	*Lbs.*	*g*	*g*		*P. ct.*
1	100 per cent rag	106	22	42.9	57.1	133	1.0	7.0	1.2	105	0.044	0.042	63	46	1,200	1,040	All satisfactory (3/16-inch mandrel).	13
2	60 per cent rag, 30 per cent newspaper, 10 per cent sawdust.	115	24	39.1	60.9	156	.9	5.8	.5	92	.052	.049	52	39	1,088	992	4 satisfactory, 1 cracked slightly (3/8-inch mandrel).	9
3	10 per cent rag, 60 per cent newspaper, 30 per cent sawdust.	110	23	42.3	57.7	136	1.5	2.2	1.2	66	.057	.054	58	44	560	608	All cracked badly (3/8-inch mandrel).	12
4	60 per cent rag, 20 per cent bagging, 20 per cent newspaper.	110	23	41.1	58.9	144	.7	6.4	1.0	107	.048	.046	66	49	912	928	3 satisfactory, 2 cracked slightly (3/8-inch mandrel).	10
5	66.7 per cent bagging, 33.3 per cent neswpaper.	106	22	37.3	62.6	168	1.3	5.5	.7	85	.046	.044	60	51	896	832	1 satisfactory, 4 cracked slightly (3/8-inch mandrel).	13
6	100 per cent bagging	110	23	35.8	64.2	179	1.0	6.8	1.2	93	.049	.047	------	------	976	1,024	2 satisfactory, 3 cracked slightly (3/8-inch mandrel).	13

B. COMMERCIAL PAPER

2	100 per cent rag	139	29	38.1	61.9	163	1.2	7.6	1.6	175	0.057	0.056	78	43	1,888	1,680	All satisfactory (1/16-inch mandrel).	28
3	60 per cent rag, 40 per cent sulphite pulp.	125	26	41.3	58.7	142	1.2	5.2	1.7	183	.053	.053	86	46	1,856	1,520	----do----	35
10	80 per cent rag, 20 per cent newspaper.	149	31	36.1	63.9	177	1.3	6.2	1.6	168	.065	.060	74	39	1,968	1,808	----do----	36
13	80 per cent rag, 20 per cent mixed paper.	139	29	37.7	62.3	165	1.2	6.5	1.4	164	.059	.058	72	37	1,968	1,616	----do----	32
17	60 per cent rag, 40 per cent bagging.	130	27	36.4	63.6	174	1.1	6.6	2.0	153	.055	.054	68	35	1,872	1,504	----do----	37
22	80 per cent rag, 20 per cent ground-wood pulp.	139	29	35.8	64.2	179	1.5	6.5	1.8	163	.062	.059	71	39	1,904	1,520	----do----	37

In the water-absorption test a weighed specimen of saturated felt is entirely immersed in water at 77° F. for 24 hours. A sheet 18 by 18 inches is used in making the test, but since the object of the test is to measure the surface absorption, the treated sheet is trimmed to 12 by 12 inches before its weight is redetermined. Moisture enters more readily through the cut edges of the sheet than through the surface itself, but experience has shown that it does not penetrate more than 3 inches for the period of time immersed in the tests. The reduction in size, therefore, eliminates the effect of seepage through the cut edges. The increase in weight is figured on the basis of the original material.

The tearing tests are new to the roofing industry. They were made with the Elmendorf tearing tester, but the standard design of this instrument is not adapted to heavy material, such as roofing and saturated felts, so a modification had to be made before these materials could be tested.[12] The modification consisted in doubling the weight of the swinging sector by the addition of a brass plate and multiplying the scale readings by 2.

VI. ASPHALT ROOFING

1. METHOD OF APPLYING ASPHALT COATING TO SATURATED FELT

The asphalt coating was applied to the saturated felt in a roofing mill using large-scale production coating equipment. The method employed was that described on page 1003.

2. ANALYSIS OF ASPHALT COATING

Analysis of the asphalt coating used (bureau and commercial felts) is included in Table 2. The test methods were the same as those described on pages 1009 and 1010.

3. MEASUREMENTS ON FINISHED ROOFING FELT

The results of the tests on the finished product are given in Table 4. The methods of test used are those described in United States Government Master Specification No. 214 and the references previously given herein.

[12] F. T. Carson and L. W. Snyder, Increasing the Capacity of the Elmendorf Tearing Tester, Paper Trade J., 86, No. 13, pp. 57-60; Mar. 29, 1928.

TABLE 4.—*Test data on finished saturated and coated felt*

A. BUREAU OF STANDARDS PAPER

Felt No.	Felt composition	Weight		Constituents				Saturation of felt	Loss on heating at 80° C. for five hours	Ash in desaturated felt	Bursting strength	Thickness		Tensile strength		Tearing strength		Pliability on ¾-inch mandrel at 10° C.	Water absorption (at 25° C. for 24 hours)
		Per 480 square feet	Per 100 square feet	Felt	Saturant	Coating	Surfacing					Saturated felt	Desaturated felt	Machine direction	Across machine direction	Machine direction	Across machine direction		
		Lbs.	*Lbs.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Points*	*Inch*	*Inch*	*Lbs.*	*Lbs.*	*g*	*g*		*P. ct.*
1	100 per cent rag	216	45	22.2	30.8	42.8	4.2	139	0.0	10.0	186	0.086	0.045	78	58	1,456	1,440	1 satisfactory, 4 cracked badly.	1.8
2	60 per cent rag, 30 per cent newspaper, 10 per cent sawdust.	206	43	24.5	41.4	31.9	2.2	169	.3	8.1	139	.087	.050	64	48	944	928	All cracked badly	.7
3	10 per cent rag, 60 per cent newspaper, 30 per cent sawdust.	197	41	23.3	36.9	37.2	2.6	157	.4	4.5	103	.088	.052	62	50	624	704	do	.0
4	60 per cent rag, 20 per cent bagging, 20 per cent newspaper.	187	39	24.3	33.8	40.9	1.0	139	.2	8.3	132	.074	.040	75	56	880	960	do	2.1
5	66.7 per cent bagging, 33.3 per cent newspaper.	192	40	21.7	36.7	38.8	2.8	169	.3	8.8	130	.085	.045	70	63	976	928	do	.0
6	100 per cent bagging	211	44	18.5	36.1	43.1	2.3	195	.1	11.0	139	.090	.045	65	52	1,120	1,152	do	.0
	B. COMMERCIAL PAPER																		
2	100 per cent rag	274	57	17.5	32.1	44.7	5.5	184	0.23	9.0	215	0.105	0.051	78	43	2,112	1,808	3 satisfactory, 1 cracked slightly, 1 cracked badly.	10
3	60 per cent rag, 40 per cent sulphite pulp.	269	56	19.7	31.9	42.4	6.0	162	.11	6.9	195	.104	.051	94	52	2,240	1,696	do	9
10	80 per cent rag, 20 per cent newspaper.	264	55	21.9	43.5	27.9	6.7	199	.00	8.2	213	.104	.063	86	49	2,896	1,888	2 satisfactory, 1 cracked slightly, 2 cracked badly.	10
13	80 per cent rag, 20 per cent mixed paper.	278	58	19.5	33.5	42.1	5.0	172	.26	8.2	209	.107	.058	80	44	2,416	1,840	3 satisfactory, 2 cracked badly.	10
17	60 per cent rag, 40 per cent bagging.	245	51	20.3	37.1	35.7	6.9	182	.25	8.0	187	.092	.054	80	45	2,160	1,488	3 satisfactory, 1 cracked slightly, 1 cracked badly.	11
22	80 per cent rag, 20 per cent ground-wood pulp.	254	53	19.4	40.4	33.3	6.9	209	.00	8.2	193	.094	.057	84	45	2,256	1,648	1 satisfactory, 1 cracked slightly, 3 cracked badly.	7

VII. COMMERCIAL ROOFING FELT

To permit comparison of the experimental felts with those produced commercially, corresponding measurements on commercial felts, produced for experimental purposes, are included in the tables.

VIII. SUMMARY

1. The data given in the tables indicate that the experimental felts made at the bureau on the small Fourdrinier paper machine compared favorably with those produced commercially on a regular felt-making machine.

2. In general, the strength was greater for the commercial than for the bureau felts. In making the comparison, however, consideration must be given to the facts that a smaller percentage of substitutes was included in the commercial felts and that these felts were much thicker, also. The tensile strength of the bureau product was more nearly uniform in the two directions of the sheet.

3. It will be observed that the experimental and commercial felts of similar fiber composition absorbed practically equal amounts of kerosene, and that the same degree of saturation should, therefore, be obtained for both.

4. The comparatively narrow width of the sheet and short length of the roll caused some inconvenience in running the bureau product over the large commercial machines used for saturating and coating the felts. Because of the fineness of the sawdust particles and the possibility that they might contain some resinous materials, it was thought that the felt containing sawdust might char or burn when subjected to the high temperature of the saturating bath. No such trouble was noted in the saturating operation, however, and apparently the sawdust remained intact.

5. As would be expected, when large amounts of substitutes were included in the fiber composition the experimental felts proved more brittle than regular roofing.

6. The absorptive quality respecting impregnation with the asphalt was as good for the bureau felts as for the commercial ones. Comparison of the theoretical maximum per cent of asphalt saturation (Table 1) with the actual per cent of asphalt in the saturated felts (Table 3) shows that the felts were all undersaturated. The actual saturation was from 81 to 89 per cent of the theoretical maximum capacity for experimental felts Nos. 1, 2, 4, 5, and 6, and 69 per cent for No. 3. Owing to the small interstices in a felt containing fine sawdust, the saturating rate would, of course, be relatively slow, and for a given time the amount of asphalt absorbed would, therefore, be less. The degree of saturation for the commercial felts was from 73 to 79 per cent.

7. Some of the substitutes—for example, bagging and sawdust—made the felts relatively more porous. Such felts absorbed more asphalt and thus afford better protection for the fibers. The greater the percentage of saturant present the more moisture-resistant and, presumably, longer-lived the felts will be in service. If in such cases the initial strength and pliability are sufficient, the felts should prove satisfactory for roofing purposes.

8. The purpose of the investigation was to ascertain whether asphalt roofing felts suffer in serviceability by the addition of substitutes for rag stock. As one of the experimental felts contained as high as 60 per cent of mixed wood-fiber papers and 30 per cent of sawdust, it appears thus far that relatively large amounts of such substitutes can be introduced into the felts without great difficulty in the manufacturing processes. The tests described give considerable information on the behavior of the experimental felts, but the effect of the substitutes on the actual durability of the finished roofing remains to be determined.

9. Additional research on the comparative durability of the felts is in progress. The study includes outdoor exposure of the test specimens and accelerated aging tests in the laboratory. The work is being continued in the chemistry division of the bureau by the research associate of the Manufacturing and Industrial Research Committee of the Asphalt Shingle and Roofing Institute.

10. If the aging tests show that the presence of the substitutes employed does not adversely affect the life of the felts, the use of such substitutes in admixture with rag stock would effect considerable economy. The lower cost of the substitute materials and the saving in time and power required for the paper-making process would both contribute materially to reduce the cost of production.

WASHINGTON, February 27, 1929.

BEARING BRONZES WITH AND WITHOUT ZINC

By H. J. French and E. M. Staples

ABSTRACT

Based on a study of the wearing properties, hardness, structure, notch toughness, and resistance to deformation at temperatures between 70° and 600° F., the bronzes in the copper corner of the copper-tin-lead system were classified according to the character of the service for which they seemed to be best adapted. A study was also made of the effects of 4 per cent zinc on the properties and applications of these bronzes.

Bronzes with less than about 4 per cent tin were considered to be unsuited for general bearing service, since they had low resistance to deformation and wore rapidly in the absence of lubrication. However, some of these alloys, such as those high in lead, should serve satisfactorily for special service involving low loads.

Bronzes with less than about 5 per cent lead appeared to be suited only for service where lubrication could be maintained. However, they should be applicable with such a restriction to a wide range of service conditions, depending upon the proportions of tin present.

Bronzes containing more than about 5 per cent lead were best able of any of the groups studied to operate for short periods in the absence of lubrication. Bronzes with 15 per cent lead were better in this respect than bronzes with 5 per cent lead, but there were no appreciable advantages apparent in raising the lead above about 15 per cent.

The addition of 4 per cent zinc to the copper-tin-lead alloys had, in general, a small influence upon the properties of the bronzes studied. With two exceptions, such changes as were observed seemed beneficial rather than detrimental for bearing service since they comprised a tendency toward higher hardness and resistance to deformation under repeated blows, lower friction, and also lower wear in the absence of oil.

Further development of methods of test for wear in the presence of lubricants may show that zinc tends to increase the weight losses and duration of the "wearing-in" period of bronze bearings, but since this is also a function of the perfection of fit such effects would be disadvantageous only in certain cases.

In general, the results seemed to justify the conclusion that the effects of zinc up to 4 per cent are generally small and may be insignificant in comparison with changes in properties quite readily produced in bronzes from variations in foundry practice. This should not be construed to apply to additions of zinc when other impurities are present.

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I. INTRODUCTION

Within the past three years an extended study was made, in cooperation with the Chicago Bearing Metal Co. and the Magnus Co., of Chicago, Ill., of the wear and mechanical properties of copper-tin-lead alloys widely used in railroad bearings. As already reported,[1] this study was made with the twofold purpose of developing a laboratory testing technique for bearing metals and of finding reasons for the wide variations in the specifications of different carriers for bearings for similar conditions of service.

The testing technique developed in the investigation did not define completely all those properties of importance for alloys intended for service in bearings, but the methods used can properly form part of a more complete testing technique, since they gave information consistent with practical experience. Therefore, more extended application is justified.

Comparisons of the different alloys were based on wear tests, single-blow impact tests on notched bars, repeated pounding tests, tension or hardness tests and microscopic examination. The wear tests were made in the Amsler wear-testing machine, and in addition to determination of weight losses, attention was given to the frictional properties (torque in the tests) and the character of the worn surfaces. Wear tests were made in the presence of a lubricant at atmospheric temperatures, and tests were also made without lubrication at atmospheric and elevated temperatures up to and including 350° F. With the exception of the hardness tests, made only at atmospheric temperatures, the various mechanical tests were carried out at temperatures up to and including 600° F.

[1] H. J. French, S. J. Rosenberg, W. LeC. Harbaugh, and H. C. Cross, Wear and Mechanical Properties of Some Railroad Bearing Bronzes at Different Temperatures, B. S. Jour. Research, 1 (RP. 2); September, 1928; also Proc., Am. Soc. Test. Matls.; 1928.

The copper-tin-lead alloys previously studied were made from commercially pure raw materials, but it is seldom practicable for economic reasons to produce bearing bronzes on a commercial basis wholly from new or "virgin" metals. The largest part of the bearings now manufactured is made of remelted bearings combined with varying amounts of shop scrap and only sufficient new metal to bring the mixtures to the required compositions.

The scrap charged in the form of unserviceable bearings is generally gathered from a multitude of sources, and not only varies in the proportions of copper, tin, and lead but also in the proportions of impurities present, such as zinc, antimony, phosphorus, iron, or nickel, etc.

The subject of impurities is, then, of primary importance in the commercial production of bearing bronzes, and specifications indicate a wide difference of opinion with respect to the maximum allowable limits for different elements. An example is found in comparison of two specifications for the well-known alloy containing 80 per cent copper, 10 per cent tin, and 10 per cent lead. As shown in Table 1, the tentative specifications of the American Society for Testing Materials for sand castings permit a maximum of 0.25 per cent zinc, while the specifications of a prominent carrier call for a zinc content between 1 and 3 per cent.

TABLE 1.—*Comparison of two specifications for bronzes containing 80 per cent copper, 10 per cent tin, and 10 per cent lead*

Element	A. S. T. M. (B-74-28 T)	Illinois Central R. R. Co.	Element	A. S. T. M. (B-74-28 T)	Illinois Central R. R. Co.
	Per cent	*Per cent*		*Per cent*	*Per cent*
Copper	79–81	79–81	Phosphorus	[1] 0.25	[1] 0.25
Tin	9–11	9–11	Aluminum	None.	----------
Lead	9–11	9–11	Sulphur	[1] .05	----------
Zinc	[1] .25	1–3	Antimony	[1] .25	----------
Iron	[1] .10	----------	Other elements	[1] .15	[1] .50
Nickel	[1] .50	----------			

[1] Maximum.

Lack of information on the effects of common impurities and the wide variations in the proportions of copper, tin, and lead specified by different purchasers for bearing metals intended for similar service resulted in the establishment of a research associateship at the National Bureau of Standards by The Bunting Brass & Bronze Co., Toledo, Ohio, for the purpose of studying the properties and applications of bearing bronzes. The tests here reported constitute the first phase of a study of this subject and relate to the properties of copper-tin-lead alloys widely used in bushings in the automotive and other industries, and to the effect of zinc on such bronzes.

II. ALLOYS STUDIED

Most of the compositions tested were selected from the group regularly manufactured by The Bunting Brass & Bronze Co. Some other alloys were included to secure a more general distribution over the copper corner of the copper-tin-lead system and thus permit comparisons on the basis of ternary diagrams. However, in most cases due regard was given in the selections to the industrial production requirements.

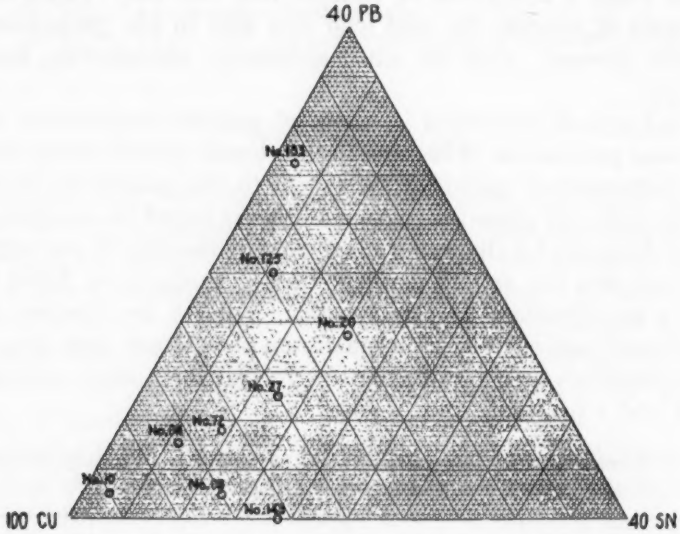

FIGURE 1.—*Ternary diagram showing location of the bronzes tested*

Two groups of alloys were prepared. The first comprised alloys of copper, tin, and lead of compositions shown in Figure 1. In the second group the copper-tin-lead ratios were kept the same, and 4 per cent of zinc was added.

It was, of course, not practicable to adhere exactly to the intended compositions in the production of the test castings, but the deviations encountered can be neglected since comparisons are based largely upon the trends in the copper-tin-lead and copper-tin-lead-zinc systems. The chemical compositions of the different test castings are summarized in Table 2.

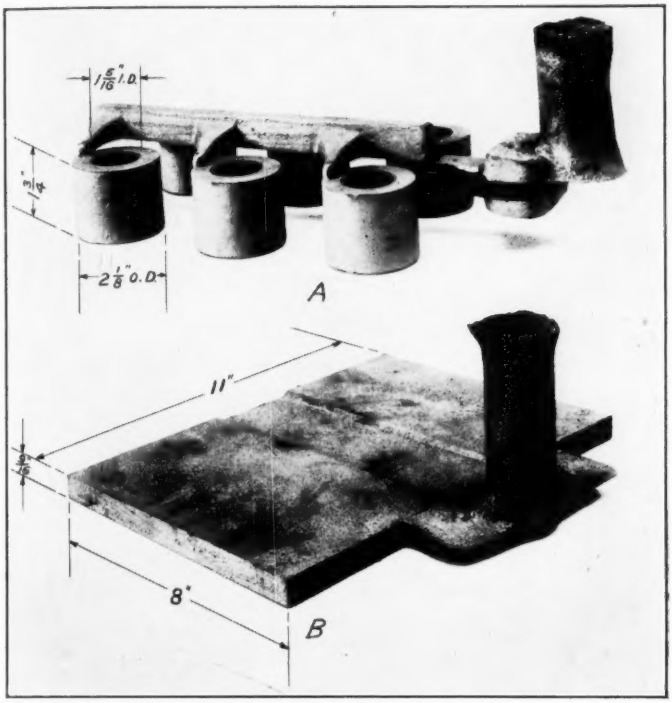

FIGURE 2.—*Test castings used*

A, for the wear-test specimens.
B, for the impact, pounding and hardness tests.

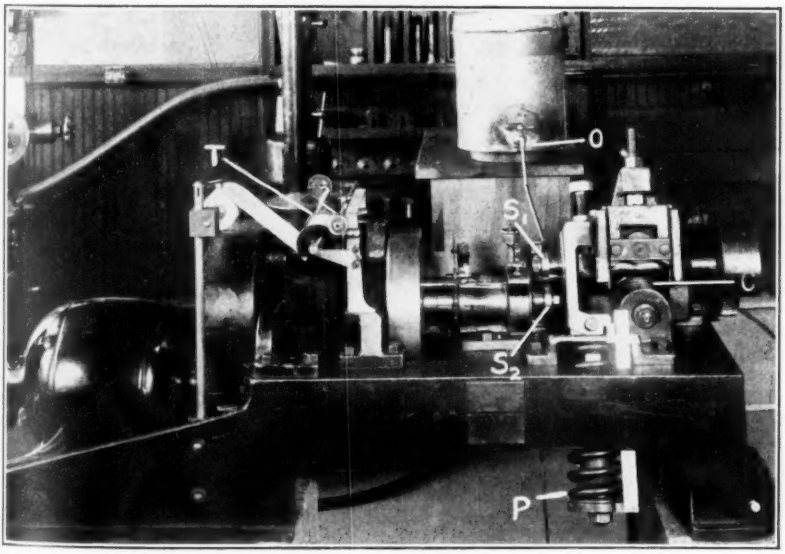

FIGURE 3.—*Amsler wear testing machine used*

Surfaces of specimens S_1 and S_2 move in the same direction but at different speeds, with lateral oscillation produced by cam C and under contact pressures controlled by spring P. The friction is recorded on the torque indicator T. In tests with lubrication the oil is supplied from reservoir O. In all tests the total load between specimens was 37.5 pounds; the slip, 12 feet per minute; the amplitude of lateral oscillation, 0.3 inch.

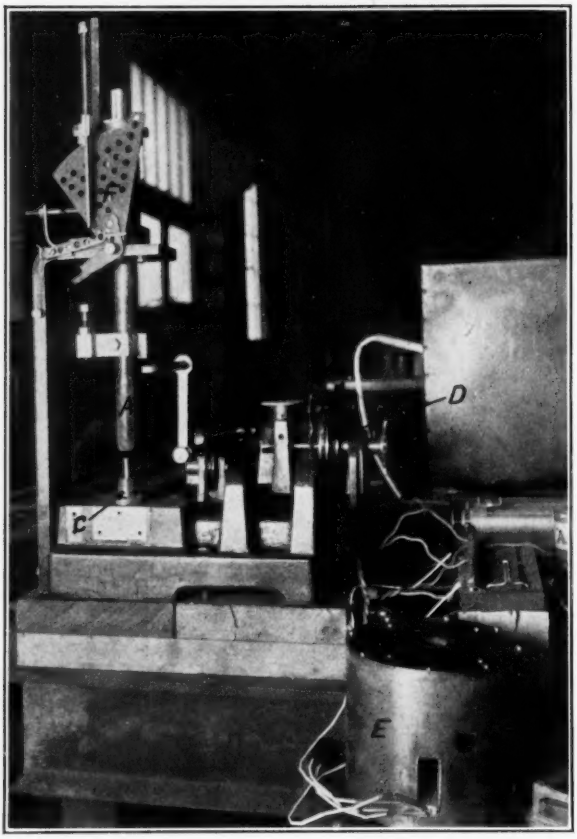

FIGURE 4.—*Equipment used in the repeated pounding tests*

Specimen *B*, on anvil *C*, is subjected to repeated blows in compression by the falling weight *A*. Furnace *E*, mounted on anvil *C*, is used for tests at elevated temperatures. *D* is the driving mechanism and *F* prevents auxiliary blows from rebound of *A*.

Tests made with a weight of 7.15 pounds falling through a distance of 2 inches.

TABLE 2.—*Chemical compositions of bronzes tested*

Alloy No.	Chemical composition [1]					Used for wear tests (W) or mechanical tests (M)
	Cu	Sn	Pb	Zn	Total	
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	
10 [2]	96.5	1.8	1.8	----------	100.1	W
10	95.4	2.1	2.0	----------	100	M
10Z [2]	91.4	2.0	1.9	4.5	99.8	W
10Z	92.5	2.0	1.8	[3] 3.7	100	M
20 [2]	73.7	11.8	14.4	----------	99.9	W
20	73.1	12.8	14.1	----------	100	M
20Z [2]	69.4	12.1	15.1	3.2	99.8	W
20Z	70.5	11.9	13.8	[3] 3.8	100	M
27	80.4	10.0	9.5	----------	99.9	W
27	79.8	10.3	9.6	----------	99.7	M
27Z	76.5	9.4	9.8	4.1	99.8	W
27Z	76.4	10.1	9.1	[3] 4.4	100	M
27 [2]	80.5	9.8	9.6	----------	99.9	W
27Z [2]	77.4	9.0	10.1	3.3	99.8	W
72	85.8	7.3	6.8	----------	99.9	W
72	85.3	7.3	7.2	----------	99.8	M
72Z	82.2	6.8	7.0	4.0	100	W
72Z	82.5	7.2	6.7	[3] 3.6	100	M
94	89.3	4.5	6.2	----------	100	W
94	89.6	4.8	5.6	----------	100	M
94Z	85.3	4.8	5.8	4.1	100	W
94Z	85.6	4.6	5.8	[3] 4.0	100	M
96	88.1	10.0	2.0	----------	100.1	W
96	88.4	10.3	1.5	----------	100.2	M
96Z	83.9	9.3	2.1	4.4	99.7	W
96Z	84.8	9.5	2.0	[3] 3.7	100	M
96 [2]	88.5	9.5	2.0	----------	100	W
96Z [2]	84.8	9.9	2.1	3.1	99.9	W
125	75.3	4.5	20.1	----------	99.9	W
125	76.6	4.6	18.9	----------	100.1	M
125Z	72.8	4.3	19.1	3.7	99.9	W
125Z	73.0	4.3	18.5	[3] 4.2	100	M
133 [2]	68.8	2.4	28.7	----------	99.9	W
133	75.2	1.5	23.2	----------	99.9	M
133Z [2]	66.3	2.2	27.8	3.7	100	W
133Z	71.0	1.4	23.8	[3] 3.8	100	M
143	85.2	14.7	----------	----------	99.9	W
143	84.8	15.0	----------	----------	99.8	M
143Z	81.1	14.5	----------	[3] 4.4	100	W
143Z	82.0	13.8	----------	[3] 4.2	100	M

[1] 24 of the samples were analyzed for P, and Sb; 12 were analyzed for Fe and S; in no case was any one of these elements present in quantities greater than 0.02 per cent.

[2] These castings in addition to those for the mechanical tests were made at the Bureau of Standards; all others were made in the foundries of The Bunting Brass & Bronze Co., Toledo, Ohio.

[3] Zinc by difference.

III. PREPARATION OF THE TEST CASTINGS

The test castings were of relatively thin sections to give structures and properties comparable to those found in the small bushings so widely used in the automotive industries. Castings for the wear-test specimens were hollow cylinders, while those used for the impact, pounding, and hardness test specimens were in the form of plates as is shown in Figure 2.

The method of preparation of the castings was substantially as follows: Approximately 1,400 pounds of copper (trolley) wire was

melted in a gas-fired furnace under a covering of limestone and borax. About 8 per cent of tin was added to the copper when melted, and, after thorough stirring, the metal was cast into small notched ingots which were used as the basis of the melts for the test castings. These ingots were melted in a small gas-fired crucible furnace, together with the required amounts of copper, tin, and lead under a limestone-borax slag. Zinc when required was added after skimming the metal. All the castings were made in sand molds. Casting temperatures were measured with chromel-alumel thermocouples and a potentiometer.

The metal was poured at approximately 2,000° F. except in the case of alloys Nos. 10 and 133. (Table 2.) A somewhat higher pouring temperature (around 2,100° F.) was required to fill the molds with sound metal with alloy No. 10 containing 96 per cent copper and 2 per cent each of tin and lead.

The large amount of lead (28 per cent) in alloy 133 made necessary the use of a somewhat lower pouring temperature, estimated around 1,950° F., in order that the copper-tin solution would freeze in the mold before the lead had a chance to segregate to any great degree. In all cases the metal was stirred continuously from the time the crucible was removed from the furnace until the metal was ready to pour.

IV. METHODS OF TEST

Metals used as bearings are subjected to a wide range of conditions in service. Failures occur by wear or by inability to carry the required loads, to withstand impact, or to resist deformation ("pounding out"). In addition to these properties, consideration should be given to the frictional properties (for example, starting torque), ability to operate at elevated temperatures, ease of manufacture, and other characteristics.

The conditions encountered in practical service are seldom simple. Most often they are such that the selection of the bearing metal is a compromise to obtain the best combination of properties. The development of a testing technique which permits a logical selection for the varied conditions of practical service is therefore not simple. The situation is further complicated by the fact that the study of the wear of bearing metals can not be divorced from that of lubrication, since most bearings are designed for service in the presence of oils, greases, or other lubricants. The conditions of lubrication encountered industrially vary from so-called complete film lubrication to practically no lubrication at all.

In this investigation wear tests were made both in the presence and absence of oil, as these relate to extreme conditions. The resistance to deformation was studied by repeated pounding tests and the brittleness by single blow impact tests on notched bars. Since

bearings are often required to operate at temperatures above atmospheric, the different tests were made at elevated as well as at atmospheric temperatures.

These methods of test are the same as those previously used and have already been described in detail.[2] Photographs of the equipment used, together with brief descriptions of the principles of operation, are given in Figures 3, 4, and 5.

Objections have been raised to the described methods of test on the basis that correct design can make the properties of the metals of construction for bearings of minor importance. Some engineers usually also favor tests of full-size bearings under practical conditions of lubrication and question the usefulness of wear tests made without lubricants.

The properties of the metals of construction for bearings probably are of minor importance in cases where complete film lubrication can be guaranteed and where also design can reduce service stresses. However, the achievement of this ideal is not always practicable for economic or other reasons, and the properties of the metals of construction still demand consideration.

While the selected methods of test do not completely characterize those properties of interest in bearing-metal applications and probably can not be justly used for fine discriminations they should enable classification of groups of metals in a way which will eliminate large numbers of alloys from consideration when attempting to select metals for definite types of service. Final selection can then be made from a smaller group by actual service tests or in other ways. In fact, the data to be discussed in this report have already been used successfully in this manner.

While questions relating to methods of test were discussed at some length in the report of preliminary work, already referred to, it may be well to point out again that two of the principal points of contention concerning the work to be reported relate to the usefulness of dry-wear tests and the adaptability of the Amsler wear testing machine to the study of bearing metals.

As has been pointed out already, the conditions of lubrication encountered industrially vary from so-called complete film lubrication to practically no lubrication at all. Quite probably much of the wear produced in practical service occurs during periods of so-called boundary lubrication. Since this is essentially an unstable condition of lubrication it does not appear practicable at this stage of the development of wear testing to obtain reproducible results under conditions of boundary lubrication. Wear is not an important factor in the presence of complete film lubrication, and therefore it seems logical to use tests without lubricants as the base line for

[2] See footnote 1, p. 1018.

present comparisons and the development of a more complete testing technique. Furthermore, the results so far obtained have in most respects been generally consistent with practical experience.

The selection of the Amsler wear-testing machine in which it is practicable to approach line contact between the bearing and shaft metals is justified by the elimination of the factor of fit. In the suggested tests of full-size bearings it is difficult to eliminate variations from the factor of fit, by which is meant variations in the initial smoothness of the contact surfaces and how well these conform one to the other. It is known that variations from these sources

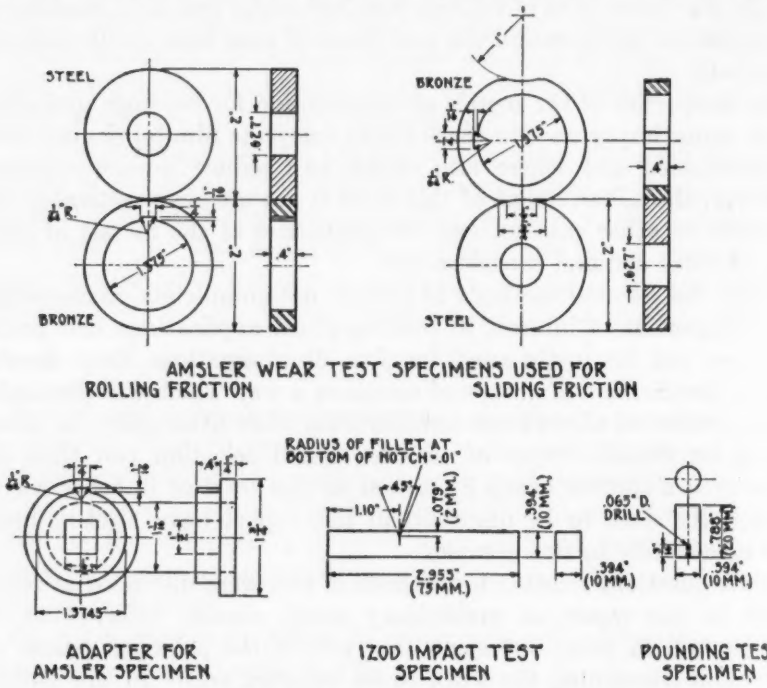

FIGURE 6.—*Test specimens used*

can materially affect the amounts and rates of wear, and the results of tests of full-size bearings are more often indicative of the manner of installation or the conditions of lubrication than of the performance of the metals.

Further development and perfection of the methods of test used in this investigation can be expected to throw further light upon justifiable interpretations of the results, but for the present the principal use of the data, and the only one recommended, is the grouping of the metals according to the broad classes of service for which they are best adapted.

The steel specimens which, for the previous wear tests, were cut from used medium carbon-steel railroad axles were replaced by

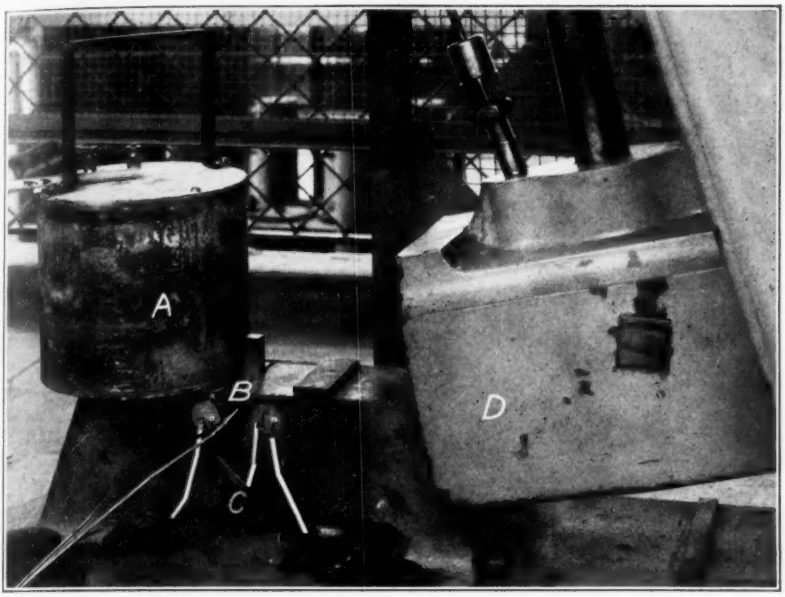

FIGURE 5.—*Part of the equipment used in the notched-bar (Izod) impact tests*

Specimen *B* is subjected to a blow from tup *D* immediately after removal of equalizing furnace *A*. The coils, *C*, permit the vise to be brought to the temperature of furnace *A*.

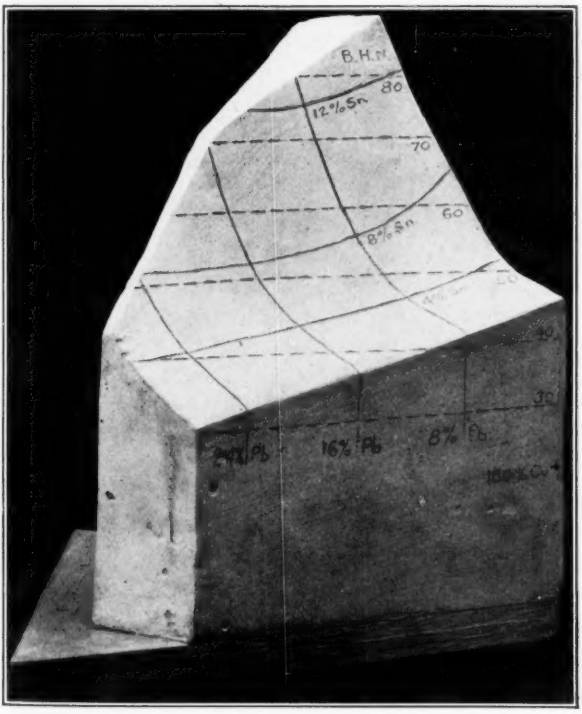

FIGURE 7.—*Approximate Brinell hardness values for part of the system copper-tin-lead*

Based on tests with a 10-mm ball and a 500-kg load

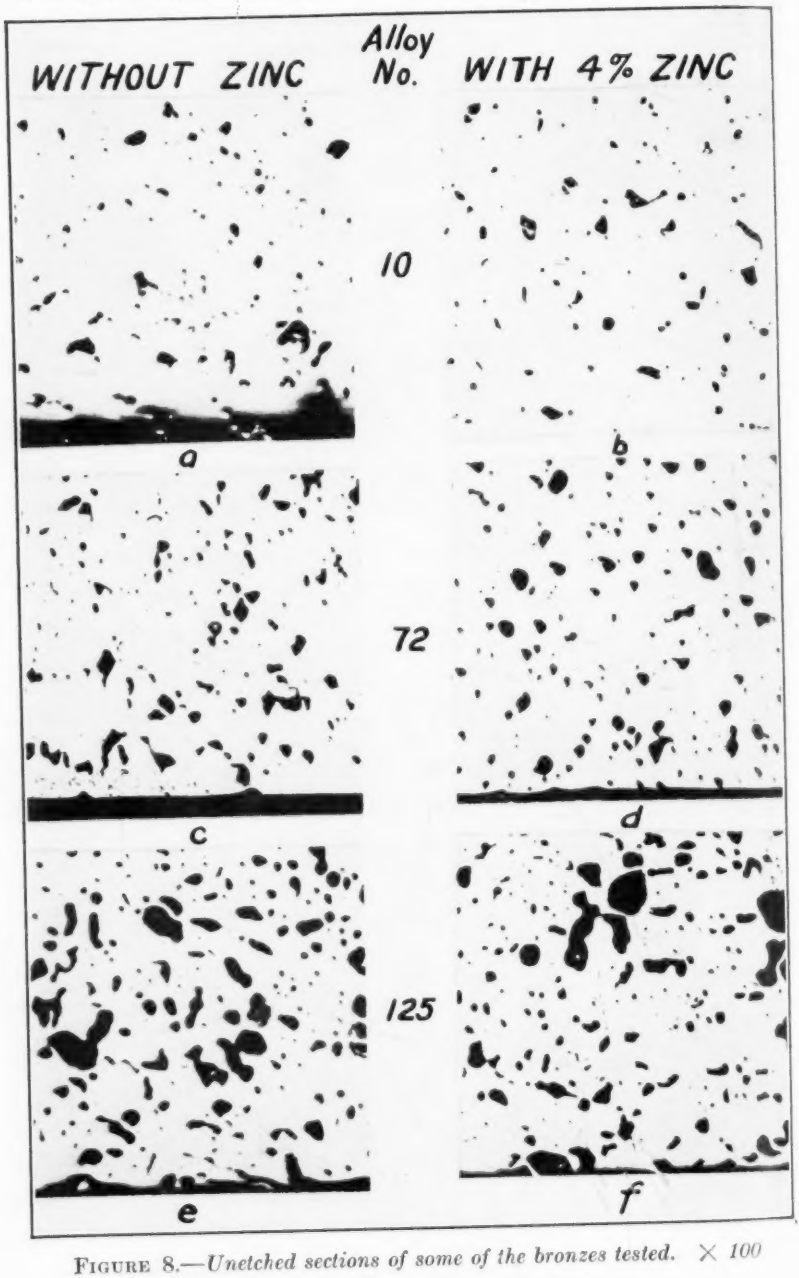

FIGURE 8.—*Unetched sections of some of the bronzes tested.* × 100

Alloy No. 10, nominally 96 per cent Cu, 2 per cent Sn, 2 per cent Pb.
Alloy No. 72, nominally 85.4 per cent Cu, 7.3 per cent Sn, 7.3 per cent Pb.
Alloy No. 125, nominally 75.5 per cent Cu, 4.5 per cent Sn, 20.0 per cent Pb.

hardened steel of the composition and heat treatment shown in Table 3.

TABLE 3.—*Composition and heat treatment of steel used in the wear tests*

	Per cent
Carbon	0. 93
Manganese	1. 11
Silicon	. 20
Chromium	. 32
Tungsten	. 36

Heat treatment:
1,500° F., 30 minutes quench in thin oil.
350° F., 1 hour quench in thin oil.
Rockwell "C" scale hardness after treatment, 61 to 63.

The selection of this steel was the result of a careful survey by The Bunting Brass & Bronze Co. of the applications of their bushings. A wide difference was found in the shafting materials, but in a majority of cases hardened steels were employed. Casehardened low-carbon steels were most often used, but as difficulties were anticipated in reproducing results with casehardened low-carbon steel specimens, the oil-hardening steel (Table 3) was selected. This selection was based on comparable surface hardness, and is considered to represent the steel contact surfaces encountered in very many of the practical applications of the bearing bronzes studied.

The test specimens used in the different tests are shown in Figure 6. They are similar to those employed in previous work, with the exception of the specimen for the repeated pounding tests, which had a ratio of length to diameter of 2 instead of 2.5. This change reduced bending of the specimens and resulted in more consistent results at large deformations.

V. EXPERIMENTAL RESULTS

1. HARDNESS AND STRUCTURE OF Cu-Sn-Pb ALLOYS

The tests on the copper-tin-lead alloys without zinc confirmed the results of previous tests [3] on a narrower range of compositions and make possible a classification of alloys over a considerable area of the copper corner of the copper-tin-lead ternary diagram. Solid models are used as the basis for discussion, since these offer a convenient means of indicating the trends produced by combined variations in the proportions of copper, tin, and lead. In these models the position of any point on the triangular base represents the chemical composition, while the height represents the particular property under discussion. General trends are shown without emphasizing

[3] See footnote 1, p. 1018.

minor variations, which are of no great practical importance and probably associated with experimental errors.

As shown in Figure 7, the hardness of the bronzes increased with increase in the proportions of tin, particularly when the alpha solid solubility of tin in copper was exceeded. For the conditions encountered in the preparation of the test castings the limit of this solubility was at about 9 per cent tin in copper, as will be evident from examination of the micrographs of Figure 9. As the lead in the bronzes increased the hardness decreased, whether the bronzes contained large or small proportions of tin. These characteristics are well known, and Figures 7, 8, and 9 are given merely as a record of the hardness and structures of the particular castings tested.

2. WEAR WITH AND WITHOUT A LUBRICANT

Before discussing the results of other tests it should be recalled that difficulties were encountered in earlier work in attempting to define the wearing properties of bronzes by tests in the presence of lubricants. These difficulties were due partly to the fact that with what was probably complete film lubrication the metals were not in continuous and direct contact and the wear dropped to such low rates after an initial "wearing-in" period that it became impracticable to differentiate with any degree of certainty between the various metals. As previously stated, there are not at present available well-defined methods for making wear tests under the unstable conditions of so-called "boundary lubrication" where wear is liable to occur in practical service, and, accordingly, the wear tests upon which the major comparisons were based were made dry: that is, in the absence of the customary lubricants.

Such tests gave only a partial picture of the wearing properties of the bronzes tested in the previous investigation and therefore further efforts were made to secure interpretable data from wear tests made in the presence of oil. Tests were continued for long periods, and the slopes of the wear-revolution and wear-work curves subsequent to the "wearing-in" period (illustrated in fig. 10) are used as the basis of Figure 11.

However, these tests can not justly be given as much weight as those made without oil, since the differences in duplicate determinations (Table 4) were more nearly of the order of magnitude of the differences between different bronzes than was the case in the dry-wear tests. This is due to the fact that in the dry-wear tests the bronzes quickly showed fairly constant and relatively high rates of wear, while in the presence of oil the first rapid wear was followed by decreases to very low wear rates. (Fig. 10.) Furthermore, while the tests with oil were continued for periods four to seven times as

long as those required to reach an actual or apparent state of equilibrium in the dry-wear tests, it is not known whether further decreases in the wear rates and a practical elimination of the differences between the different bronzes would result if the tests in the presence of oil were continued for even longer periods.

TABLE 4.—*Summary of the results of wear tests with lubrication*

Lot No.	Chemical composition				Rate of wear after initial period, weight loss per—		Total number [1] of revolutions (in thousands)	Total [1] work done (in 1,000 m kg)	Total [1] weight loss (in g)
	Cu	Sn	Pb	Zn	1,000 m kg	10,000 revolutions			
	Per cent	*Per cent*	*Per cent*	*Per cent*					
BRONZES WITH LESS THAN 5 PER CENT LEAD									
11D3	85.2	14.7			0.0019	0.0021	100	10.6	0.07
11D4	85.2	14.7			.0026	.0033	160	19.0	.45
12D3	81.1	14.5		4.4	.0027	.0039	340	47.6	1.05
7D3	88.1	10.0	2.0		.0031	.0033	120	14.6	.15
15D3	96.5	1.8	1.8		.0028	.0032	90	10.2	.05
16D3	91.4	2.0	1.9	4.5	.0031	.0042	330	43.8	.89
Average					.0027	.0033			
BRONZES WITH 5 TO 12 PER CENT LEAD									
1D3	80.4	10.0	9.5		0.0025	0.0027	120	13.9	0.11
3D3	85.8	7.3	6.8		.0034	.0042	120	14.3	.25
3D4	85.8	7.3	6.8		.0017	.0022	120	15.3	.33
5D3	89.3	4.5	6.2		.0019	.0025	120	14.7	.14
Average					.0024	.0029			
BRONZES WITH 15 PER CENT OR MORE LEAD									
17D3	73.7	11.8	14.4		0.0042	0.0052	160	19.3	0.51
18D3	69.4	12.1	15.1	3.2	.0010	.0013	260	34.1	.56
9D3	75.3	4.5	20.1		.0040	.0042	100	11.1	.08
9D4	75.3	4.5	20.1		.0042	.0053	160	19.7	.49
23D3	68.8	2.4	28.7		.0071	.0089	120	13.2	.25
24D3	66.3	2.2	27.8	3.7	.0048	.0060	340	45.0	1.71
Average					.0042	.0052			

[1] When the tests were discontinued.

An adequate testing technique has not yet been developed for wear of bearing bronzes in the presence of lubricants, and while the individual differences shown in Table 4 were disregarded and the average wear rates of groups of bronzes made the basis of the smooth contours of the solid model shown in Figure 11, some definite trends are shown which can justly be considered along with the results of the dry-wear tests.

Aside from the very low rates of wear shown by all the bronzes subsequent to the "wearing-in" period, it will be observed that the high-lead bronzes wore somewhat more rapidly in the presence of oil than did the low-lead bronzes. This is directly opposite to the effects observed in the absence of oil.

The addition of 4 per cent zinc to the copper-tin-lead alloys did not produce outstanding differences in the wear rates subsequent to the "wearing-in" period in the tests made with oil. However, the weight losses and the durations of the "wearing-in" periods were generally greater in the bronzes with zinc than in the corresponding

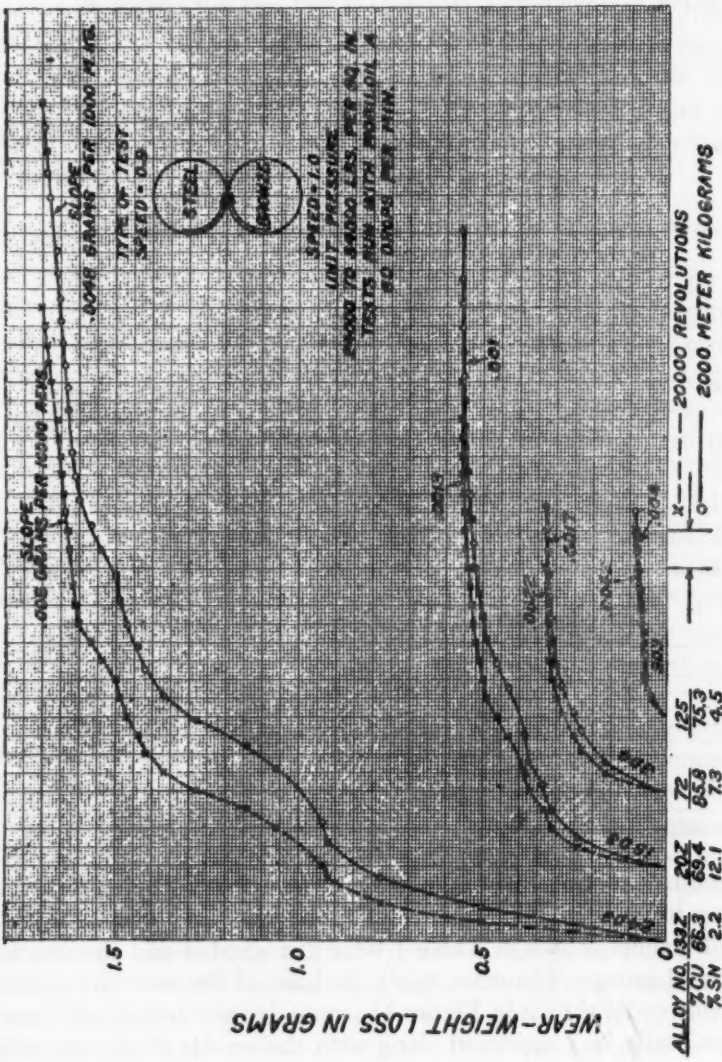

FIGURE 10.—*Relations between wear, work, and revolutions in wear tests made in the presence of oil*

alloys without zinc. This might be given more weight were it not for the fact that the bronzes with zinc were cast, machined, and tested some months after those without zinc. The "wearing-in" period in tests made in the presence of oil is known to be dependent quite largely upon the smoothness of the original contact surfaces, the oil,

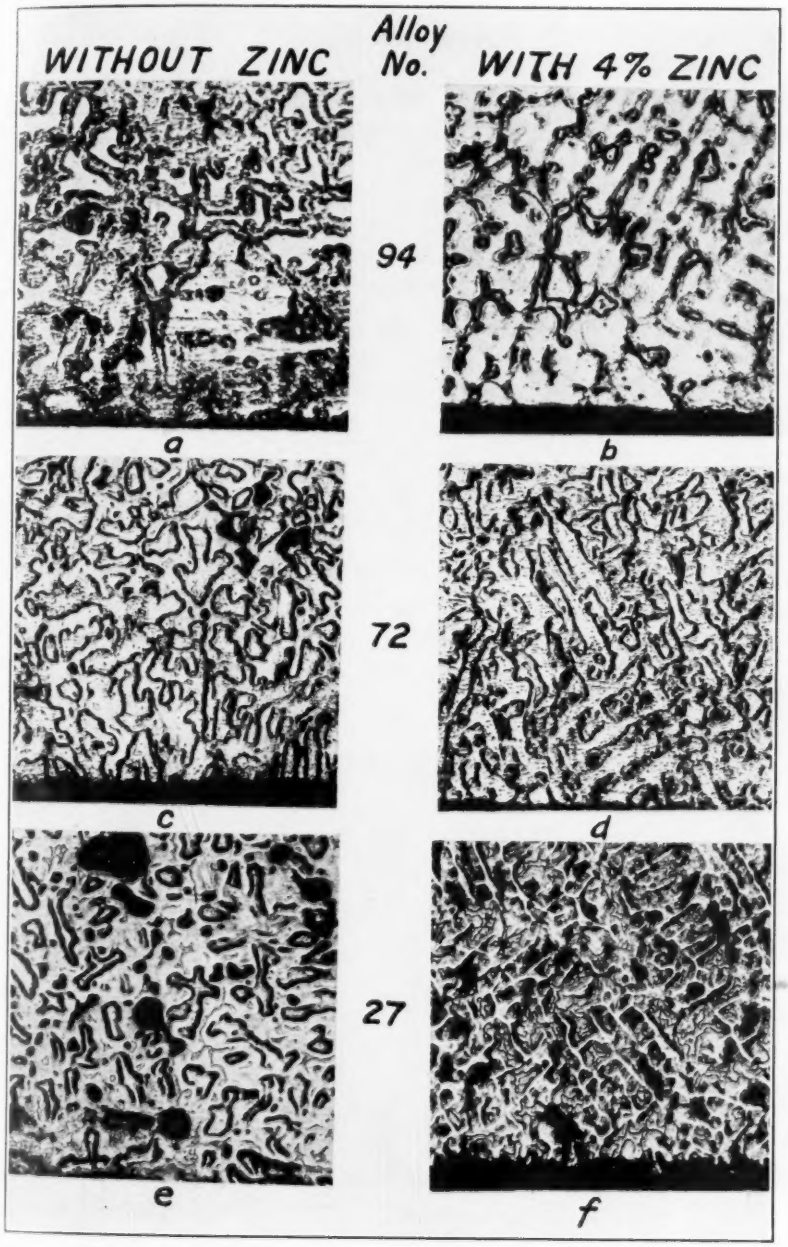

FIGURE 9.—*Micrographs of some of the bronzes tested.* × *100*

Etched with solution of 3 parts NH_4OH plus 1 part H_2O_2 followed by solution of $FeCl_3$ in HCl. (10 g $FeCl_3$ plus 30 ml conc. HCl plus 120 ml H_2O).
Alloy No. 94, nominally 89.4 per cent Cu, 4.5 per cent Sn, 6.1 per cent Pb.
Alloy No. 72, nominally 85.4 per cent Cu, 7.3 per cent Sn, 7.3 per cent Pb.
Alloy No. 27, nominally 80.0 per cent Cu, 10.0 per cent Sn, 10.0 per cent Pb.

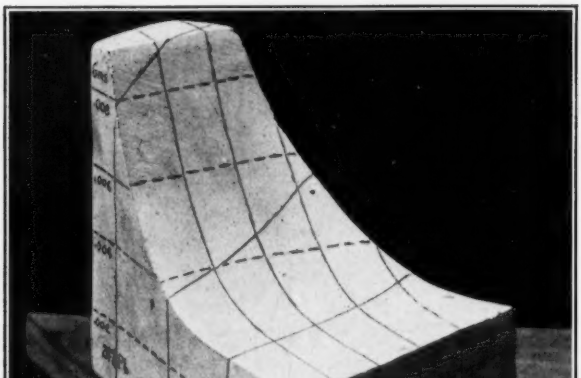

FIGURE 11.—*Wear (subsequent to the "wearing-in" period) of the bronzes tested with lubrication at atmospheric temperatures*

Wear expressed in weight loss per 10,000 revolutions. Conditions of test, including the oil used, are described in detail in the reference given in footnote 1 of the text.

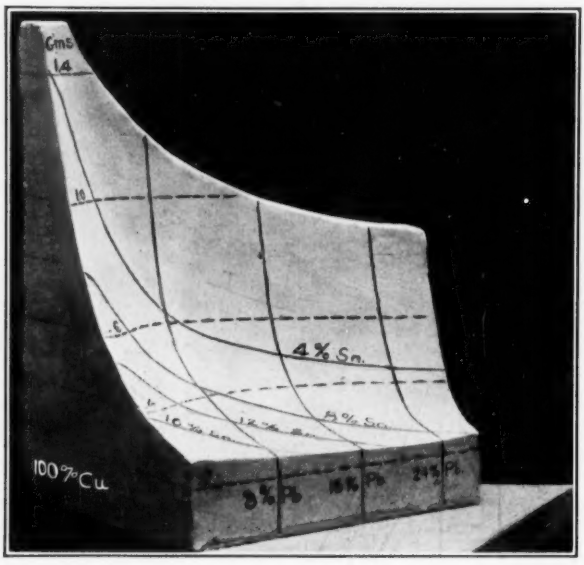

FIGURE 12.—*Wear of the bronzes tested without lubrication at atmospheric temperatures*

Wear expressed in weight loss per 10,000 revolutions. Conditions of test are described in detail in the reference given in footnote 1 of the text.

the metals themselves, and other factors, including contact pressures and rates of slip. Since the bronzes with and without zinc were not all prepared and tested at one time, the described differences in performance may not be the result solely of the additions of zinc.

But even if the results of the wear tests with oil are assumed to establish that zinc tends to increase the weight losses and duration of the "wearing-in" period zinc will not necessarily exert a deleterious effect upon bronzes used in bearings, since the importance of the "wearing-in" period is a function of the fit. The better the fit—that is, the smoother the original surfaces and the better the conformity of bearing and shaft—the less will be the practical importance of the "wearing-in" period and the effects of the zinc.

With the possible exception of variations in the "wearing-in" period, the wear tests made in the presence of oil developed no deleterious effects from the addition of 4 per cent zinc to the copper-tin-lead alloys. In this respect the tests with oil gave similar results to the majority of those tests made without oil, which will be described subsequently in this report.

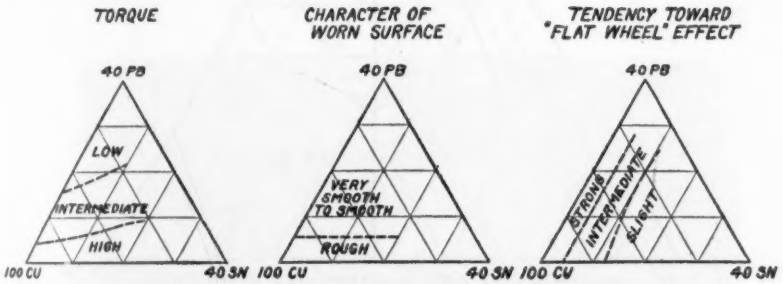

FIGURE 13.—*Special features observed in the wear tests without lubrication at atmospheric temperatures*

3. TRENDS IN THE Cu-Sn-Pb SYSTEM

Figure 12 shows that the rates of wear of the bronzes in the absence of oil were lowered by increase in either tin or in lead. However, the alloys with less than about 4 per cent tin are not well suited for general bearing service, since their wear rates remained relatively high even in the presence of appreciable proportions of lead. As is shown in Figures 13 and 14 (*a*), alloys with less than about 4 per cent tin also showed a strong tendency toward "flat wheel" effects which may be taken to indicate low resistance to deformation. This is confirmed in Figure 15, in which are summarized the results of the repeated pounding tests.

Thus a twofold advantage was gained from the addition of the tin to copper in that the rate of wear was reduced and the strength or resistance to deformation was increased. On the other hand, the cop-

per-tin alloys low in lead had relatively unfavorable frictional properties, as is shown by the high torque values (fig. 13), and also acquired rough-worn surfaces (fig. 14 (*b*)). The worn surfaces of the alloys high in lead were relatively smooth (fig. 14 (*c*)) and the friction was relatively low. Both of these latter characteristics are favorable in preventing damage during any temporary inadequacy in lubrication. High friction will tend to increase the operating temperatures and to accelerate wear and should also promote seizures; rough-worn surfaces may increase tendencies to score the shaft.

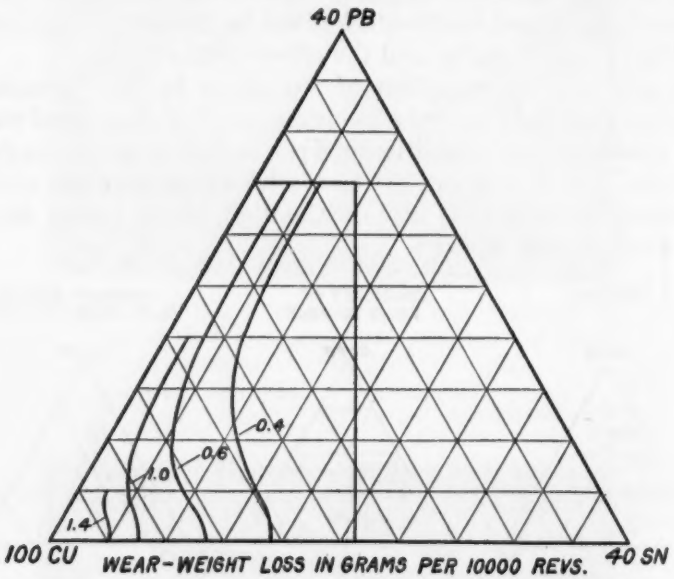

FIGURE 17.—*Contours of the solid model shown in Figure 12*

Conditions of test are described in detail in the reference given in footnote 1 of the text.

While increases in either lead or in tin produced progressive decreases in the wear rates, these metals can not be added in any proportions within the limits investigated without materially affecting other properties of interest in the application of bronzes in bearings. Figure 15 shows that increase in lead had only a minor effect upon the resistance to deformation under repeated blows in compression while tin markedly increased it. However, with more than about 7 or 8 per cent tin, which resulted in the appearance of the alpha-delta eutectoid, there was a general decrease in the notch toughness. (Fig. 16.) In alloys within the solid solution range increase in lead also decreased the notch toughness appreciably, but in the high tin alloys the tin effectively reduced the impact values so that the effect of the increase in lead was not so noticeable.

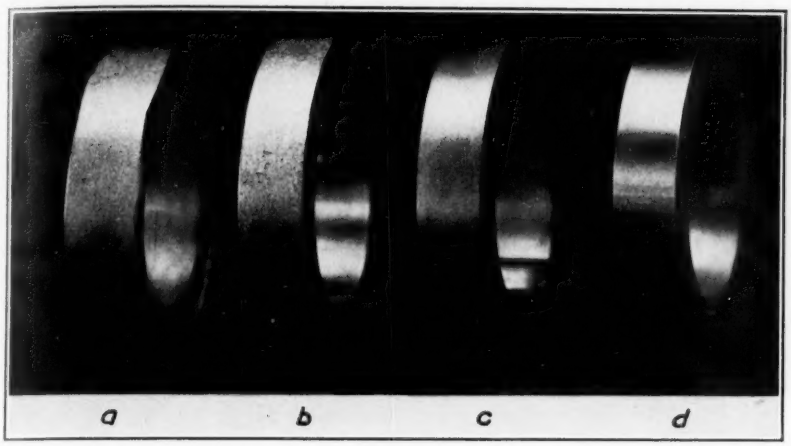

FIGURE 14.—*Photographs of some of the wear-test specimens before and after test*

a, "Flat wheel" condition in one of the bronzes tested (alloy No. 10Z); *b*, Bronze specimen showing rough type of wear (alloy No. 143); *c*, Bronze specimen showing smooth type of wear (alloy No. 20); *d*, Bronze specimen before test (machined surface) (alloy No. 96).

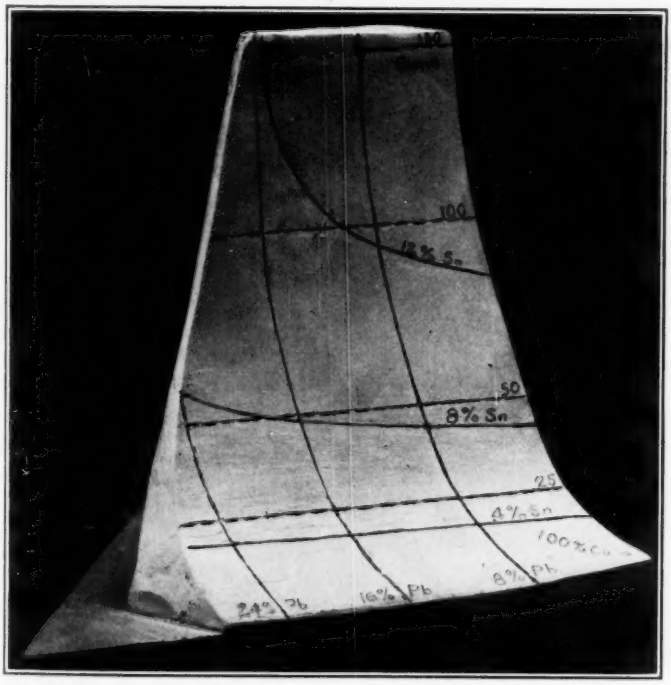

FIGURE 15.—*Resistance to repeated blows in compression of the bronzes at atmospheric temperatures*

Comparisons are based on the number of blows producing 3 per cent deformation

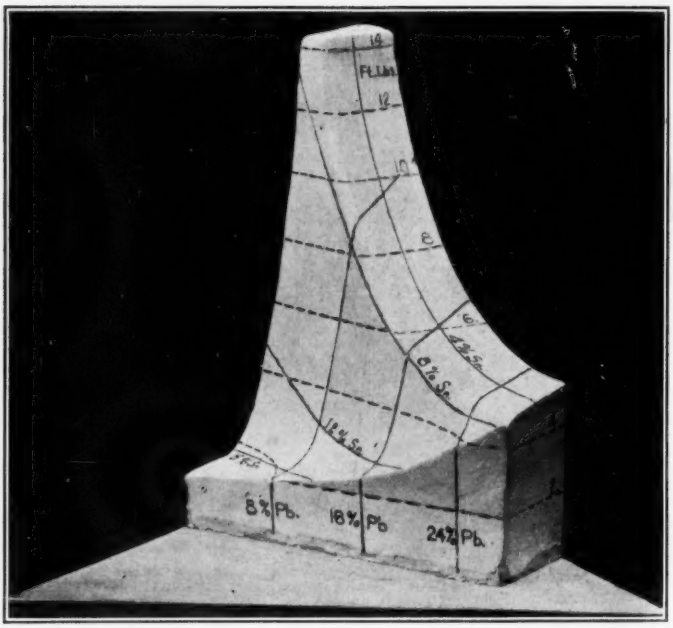

FIGURE 16.—*Izod impact resistance of the bronzes at atmospheric temperatures*

4. PRACTICAL INTERPRETATION OF THE RESULTS FOR Cu-Sn-Pb ALLOYS

Whether or not one composition may be considered to be superior to another is largely a question of the properties necessary to defeat the destructive forces encountered. Figures 17 and 18 show the contour lines of the solid models of Figures 7, 12, 15, and 16, and are included to permit comparisons of the numerical values obtained in the tests of the different alloys

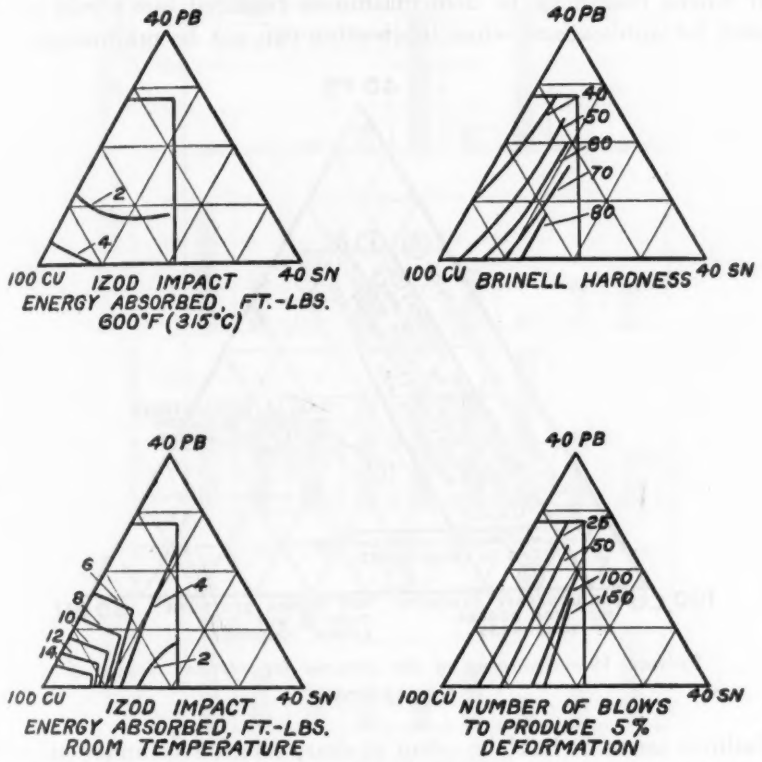

FIGURE 18.—*Contours of the solid models shown in Figures 7, 15, and 16*

From the viewpoint of practical bearing applications the copper-tin-lead alloys may be divided roughly into five groups, as is shown in Figure 19.

Group A.—The first group, comprising alloys with less than about 4 per cent tin, is unsuited for general bearing service, since the alloys had very low resistance to deformation and wore rapidly in the absence of lubrication. Other reasons are shown in the various charts in this report. However, some of these alloys, such as those high in lead, may serve satisfactorily for service involving low loads.

Group B.—This group, comprising alloys with less than about 5 per cent lead and up to about 11 per cent tin, appears to be suited for ordi-

nary conditions of service where neither very high strength nor the ability to operate in the absence of lubrication are required. The alloys were relatively tough, as judged by the Izod impact test, and those with the highest proportions of tin had moderately high resistance to deformation (strength).

Group C.—Alloys in Group C, containing from about 11 to 15 per cent tin and less than about 5 per cent lead, were stronger but had a lower notch toughness than alloys of Group B. They should serve well where resistance to deformation is required but would not be chosen for applications when lubrication can not be maintained.

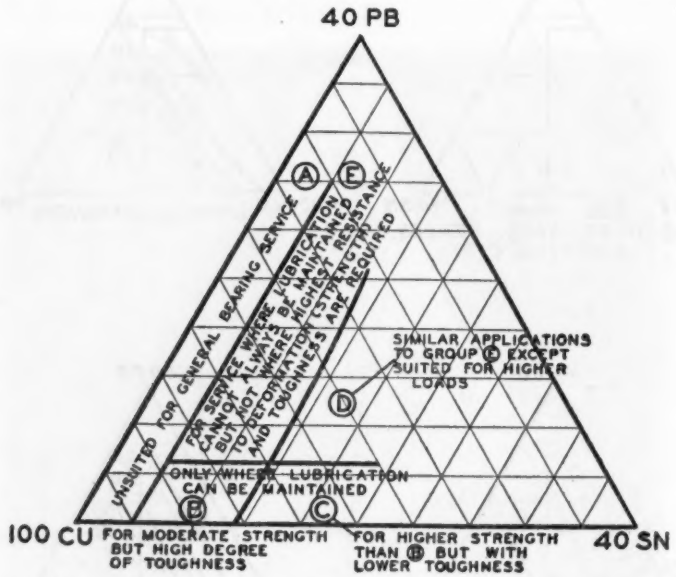
40 PB
A
E
UNSUITED FOR GENERAL BEARING SERVICE
FOR SERVICE WHERE LUBRICATION CANNOT ALWAYS BE MAINTAINED BUT NOT WHERE HIGHEST DEFORMATION RESISTANCE AND TOUGHNESS ARE REQUIRED
SIMILAR APPLICATIONS TO GROUP E EXCEPT SUITED FOR HIGHER LOADS
D
ONLY WHERE LUBRICATION CAN BE MAINTAINED
B
C
100 CU
FOR MODERATE STRENGTH BUT HIGH DEGREE OF TOUGHNESS
FOR HIGHER STRENGTH THAN B BUT WITH LOWER TOUGHNESS
40 SN

FIGURE 19.—*Grouping of the bronzes for various classes of bearing service*

Failures are more liable to occur at sharp oil grooves under suddenly applied loads than in the case of Group B alloys, expecially those with the lowest proportions of tin.

Groups D and E.—Alloys in these two groups are best able of any of the alloys tested to operate for short periods in the absence of lubrication. They contain from about 4 to 16 per cent tin and from 5 to 30 per cent lead. As a group the alloys did not have a high degree of notch toughness, but they had good resistance to deformation which increased with the proportion of tin. The alloys in these two groups had favorable frictional properties (low torque and smooth worn surfaces), especially when the lead was at the upper limits of the range. High lead tended to reduce the strength and notch toughness, but appreciable variations can be secured in the mechanical properties of the group while maintaining a desirable set of wearing properties.

5. EFFECT OF TEMPERATURE ON THE PROPERTIES OF Cu-Sn-Pb ALLOYS

The data given in support of the preceding discussion were obtained in tests at atmospheric temperatures, but the grouping of the alloys and the general conclusions relating to their fields of application apply, with few exceptions, at elevated temperatures. The results

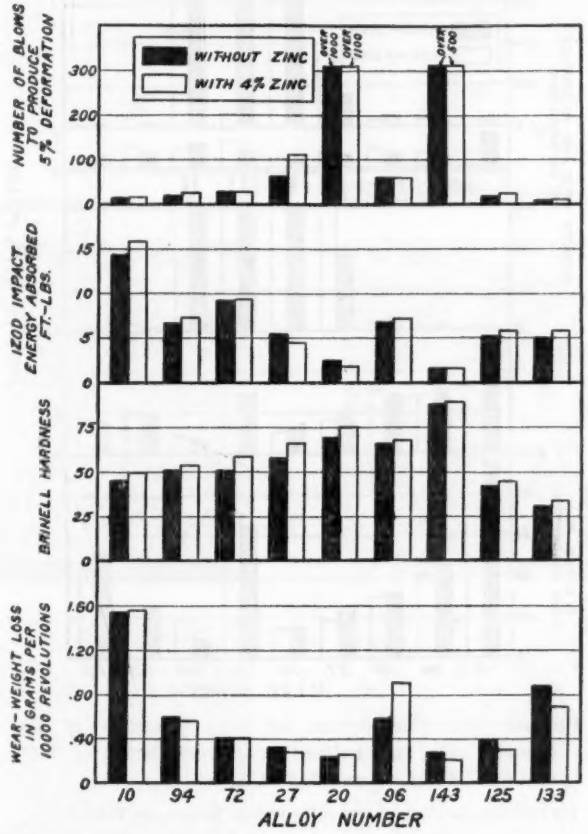

FIGURE 20.—*Comparison of the properties of the bronzes with and without zinc when tested at atmospheric temperatures*

For the chemical compositions of the various bronzes, see Table 2.

of the tests at elevated temperatures differed numerically from those at atmospheric temperatures, but the trends in the copper-tin-lead system were generally similar. Increase in temperature raised the wear rates and lowered the notch toughness, but the pounding resistance was not appreciably affected within the range 70° to 600° F. These features can be substantiated by comparison of Figures 20 and 21.

An important effect of temperature increase was to reduce the notch toughness of all the alloys to very low values. In other words, the differences in Izod impact values between the different alloys at atmospheric temperatures disappeared almost entirely when the temperature was raised to 600° F. (Fig. 18.)

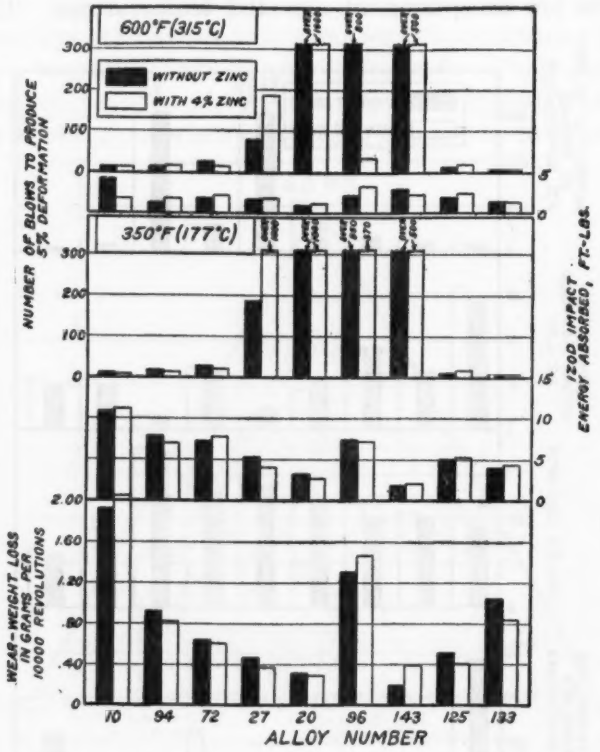
600°F(315°C)
WITHOUT ZINC
WITH 4% ZINC
350°F(177°C)
NUMBER OF BLOWS TO PRODUCE 5% DEFORMATION
IZOD IMPACT ENERGY ABSORBED, FT.-LBS.
WEAR-WEIGHT LOSS IN GRAMS PER 10000 REVOLUTIONS
10 94 72 27 20 96 143 125 133
ALLOY NUMBER

FIGURE 21.—*Comparison of the properties of the bronzes with and without zinc when tested at 350° and 600° F. (175° and 315° C.)*

For the chemical compositions of the various bronzes, see Table 2.

6. EFFECT OF 4 PER CENT ZINC ON THE PROPERTIES OF Cu-Sn-Pb ALLOYS

Zinc when added in small amounts to copper-tin alloys acts as a deoxidizer, and the resultant castings are generally freer from oxides and blowholes than untreated metal. When present in quantities greater than 2 or 3 per cent, zinc is generally considered to have a deleterious effect on the strength and ductility of bronzes. However, copper-tin-zinc alloys are widely used industrially and some have very excellent properties. The work of Hoyt,[4] Guillet and Revillon,[5]

[4] S. L. Hoyt, On the Copper-Rich Kalchoids, J. Inst. Metals, **10**, p. 235; 1913.

[5] L. Guillet and Revillon, Determination of the Coefficient of Equivalence for Special Bronzes, Rev. Met. Mem., **7**, p. 429; 1910.

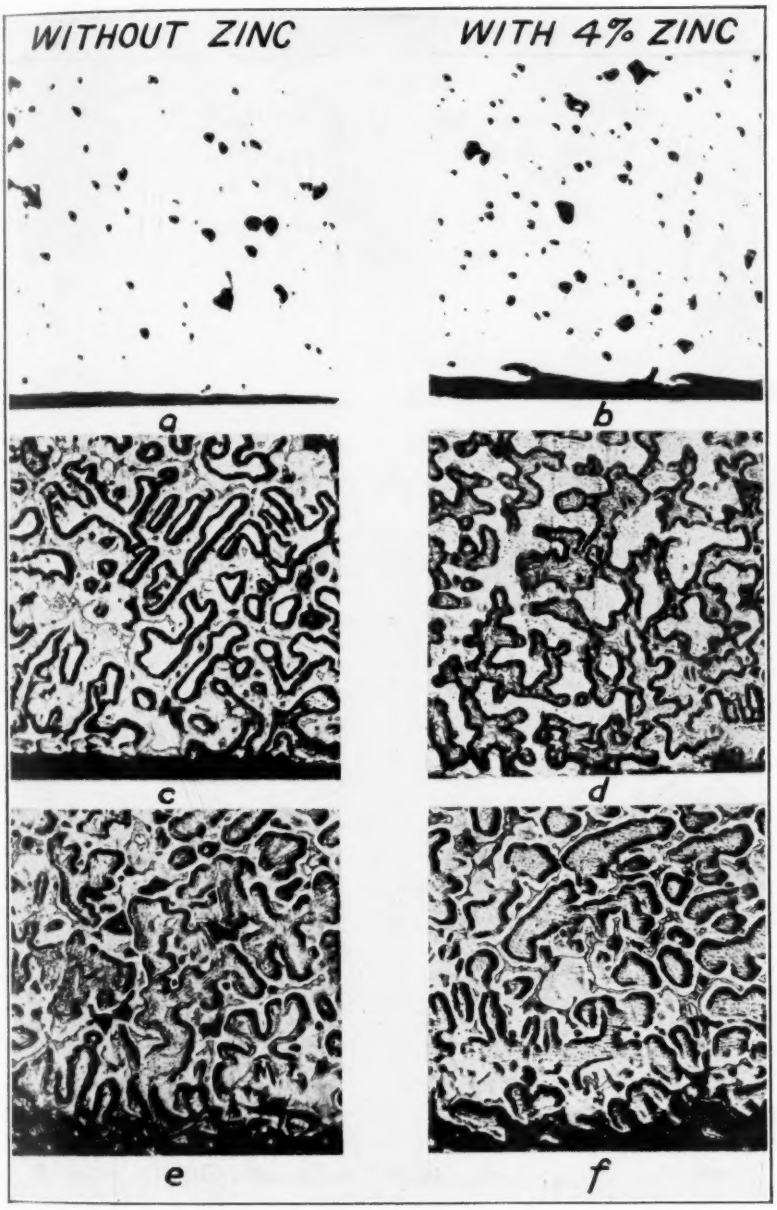

FIGURE 22.—*Micrographs of different melts of alloy No. 96 with and without zinc.* × *100*

a to *d*, inclusive, are from the first two melts; *e* and *f* are from the third and fourth melts. Etchant for *e* to *f*, inclusive, same as that described in legend for Figure 9.

and Thurston,[6] gives a fairly complete picture of the constitution and properties of alloys in this system, but much less is known of the effect of zinc on the copper-tin-lead alloys so widely used as bearing metals.

Clamer [7] found that the addition of zinc to leaded bronzes hardened the alloys considerably, embrittled them and increased the wear, but he concluded that the alloys having approximately 5 per cent tin, up to 20 per cent lead, and up to 5 per cent zinc should be entirely satisfactory for all classes of car journal bearings.

In studying the copper corner of the copper-tin-zinc system Kuhnel and coworkers [8] found that a copper-base alloy containing 9 per cent zinc and 6 per cent tin was more resistant to wear than one containing 8 per cent tin and 3.5 per cent [9] zinc.

The addition of 4 per cent zinc to the copper-tin and copper-tin-lead alloys previously discussed in this report resulted in the following effects which are shown graphically in Figures 20 and 21.

Hardness.—A measurable but slight increase was produced in the Brinell hardness.

Structure.—The zinc increased the amount of the eutectoid, as will be seen in Figures 9 (*a*) to 9 (*f*) inclusive, and in this respect may be considered to replace tin although not in equal proportions. Zinc also appeared to promote uniformity in the distribution of the lead with respect to both size and location of the particles, but this was evident only in the low-lead bronzes (fig. 8 (*c*) and (*d*)) and not in the high-lead bronzes (fig. 8 (*e*) and (*f*)). Further work would be necessary to establish the magnitude of the effects in this direction.

Impact.—Comparatively minor changes were produced in the Izod impact test values. In some cases the alloys with zinc showed slightly higher impact resistance and in others lower values than the corresponding zinc-free alloys, but the differences were small at all temperatures between 70° and 600° F., and should not affect the selection of any one of the metals for bearing service.

Repeated pounding.—Small changes were observed in the resistance to repeated blows in compression, but the tendency was generally toward an increase in the resistance to deformation at each test temperature including 600° F.

In Figure 21 there is a large difference in the numerical values used in comparing alloy No. 96 with and without zinc at 600° F. This difference is not indicative of a large difference in the resistance to deformation but is the result of the method of comparison employed, which is based on the number of blows producing 5 per cent deformation of the test specimens.

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[6] R. H. Thurston, Materials of Engineering, Pt. III, Brasses, Bronzes. John Wiley & Sons, p. 172; 1900.

[7] G. H. Clamer, Effect of Changes in the Composition of Alloys Used by the American Railways for Car Journal Bearings, Trans. Am. Inst. Metals, **9**, p. 241; 1915.

[8] R. Kuhnel, On the Constitution and Properties of Red Brass, Zeit. f. Met., **18**, p. 306; 1926; J. Inst. Metals, No. 1, p. 465; 1927.

[9] Both bronzes contained 2 per cent lead and small amounts of nickel and iron.

It so happened that the bronze with zinc deformed about 6 per cent and that without zinc only about 3½ per cent in the first 50 blows. Both then showed evidence of strain hardening, with the result that the bronze without zinc required a very large number of blows to produce 5 per cent deformation. Actually the deformational characteristics of the alloy No. 96 were quite similar with and without zinc, as is shown by the fact that at the end of 1,000 blows the bronze without zinc had deformed 5 per cent and that with zinc 7.5 per cent.

TABLE 5.—*Frictional properties of bronzes with and without 4 per cent zinc as determined in wear tests without lubrication at different temperatures*

TESTS AT ROOM TEMPERATURE

Alloy No.[1]	Total work in 1,000 M kg, done at the end of the first 40,000 revolutions		Alloy No.[1]	Total work in 1,000 M kg, done at the end of the first 40,000 revolutions	
	Alloy without zinc	Alloy with 4 per cent zinc		Alloy without zinc	Alloy with 4 per cent zinc
10	26.5	24.8	96	29.8	26.5
94	22.3	21.8	143	46.6	41.8
72	21.5	21.0	125	18.9	19.5
27	24.1	20.1	133	15.0	14.3
20	23.2	21.8			

TESTS AT 350° F.

10	[2] 17.5	[2] 15.0	96	21.0	20.0
94	20.5	16.0	143	40.4	36.2
72	18.5	17.2	125	14.0	12.2
27	17.0	16.0	133	14.5	14.5
20	19.0	19.0			

[1] See Table 2 for chemical compositions.

[2] For first 30,000 revolutions.

Wear and friction.—The zinc quite generally lowered the friction in the wear tests made without oil, as is indicated by the work values recorded in Table 5, but seemed to exert an irregular influence upon the wear rates. In a majority of cases the weight losses were not appreciably different in the corresponding alloys with and without the zinc, but in alloys Nos. 125 and 133 containing high lead and low tin (2 to 4.5 per cent tin) the zinc produced a definite decrease in the weight losses. On the other hand, in the high-tin low-lead bronzes, Nos. 96 and 143, the addition of 4 per cent zinc increased the wear rates at one or both test temperatures. The increase was especially marked in alloy No. 96 containing 88 per cent copper, 10 per cent tin, and 2 per cent lead, although the concordance of duplicate determinations was not so good as with most of the other alloys.

A second lot of castings was made of alloy No. 96 and, as in the first group, zinc increased the rate of wear. Microscopic examination showed no features to which the reversal in the effects of zinc could justly be ascribed. As is shown in Figures 22 (*a*) and 22 (*b*), a

reasonably uniform distribution of the lead particles was found, both in the alloys with and without zinc, and the structures in the two lots of each alloy were quite similar. (Figs. 22 (*c*) to (*f*), inclusive.) It may be significant that while more of the eutectoid was shown by the alloy with zinc in the second group of castings the opposite was true in the first group. (Figs. 22 (*c*) and (*d*).) This does not explain the differences in wearing properties, since in both groups the alloy with zinc showed the higher wear. However, it does indicate that the alloy under discussion is sensitive to casting conditions, and examination of Figure 12 will show that this composition is also in a field of rapidly changing wear rates.

Karr [10] showed that variations in the casting conditions might have an appreciable effect upon the properties of bronzes. Similarly, the fact that very marked changes in properties can be encountered as the result of relatively small differences in a variable, such as casting temperatures, is shown by the results reported more recently by Rowe [11] for an alloy containing 88 per cent copper, 6 per cent tin, and 6 per cent zinc.

When these effects are viewed in the light of the generally small changes produced by zinc over the greater portion of the field covered in the system copper-tin-lead, it would seem justifiable to draw the conclusion that the effects of zinc up to 4 per cent are small and may be insignificant in comparison with changes in properties quite readily produced from variations in the casting conditions.

While the foregoing comparisons of the wearing properties of the bronzes in the absence of lubrication are based on the weight losses per 10,000 revolutions, similar effects are shown when comparisons are based on the wear per unit of work. It was therefore unnecessary to include both sets of comparisons in this report.

It should also be noted that no measurable wear was produced on the steel specimens in any of the wear tests at atmospheric temperatures or 350° F. In most cases the steel specimens gained a little in weight through the adherence of bronze particles.

VI. SUMMARY

Based on hardness tests, Izod impact tests, repeated pounding tests, and wear tests, both with and without lubrication, at temperatures within the range 70° to 600° F., the bronzes in the copper corner of the copper-tin-lead system have been classified according to the character of service for which they seem to be best adapted.

Bronzes with less than about 4 per cent tin are unsuited for general bearing service, since they had low resistance to deformation and wore rapidly in the absence of lubrication. However, some of these alloys,

[10] C. P. Karr, Standard Test Specimens of Zinc Bronze, B. S. Tech. Paper, No. 59; 1916.

[11] F. W. Rowe, The Effect of Casting Temperature on the Physical Properties of a Sand-Cast Zinc-Bronze, J. Inst. of Metals, 31, p. 217; 1924.

such as those high in lead, can serve satisfactorily for special service involving low loads.

Bronzes with less than about 5 per cent lead appear to be suited only for service where lubrication can be maintained. However, they are applicable with such a restriction to a wide range of service conditions depending upon the proportions of tin present. With low tin the alloys were tough but did not resist deformation as well as the bronzes high in tin.

Bronzes containing more than about 5 per cent lead are best able of any of the groups studied to operate for short periods in the absence of lubrication. Bronzes with 15 per cent lead are better in this respect than bronzes with 5 per cent lead, but there were no appreciable advantages apparent in raising the lead above about 15 per cent. In fact, some disadvantages were encountered in that the toughness was decreased in bronzes containing around 4 to 8 per cent tin. However, by varying the proportions of tin and lead in the bronzes of this group, varied mechanical properties can be obtained while maintaining good frictional properties.

The addition of 4 per cent zinc to the bronzes had, in general, a small influence upon the properties of the bronzes studied. With two exceptions such changes as were observed seemed beneficial rather than detrimental for bearing service, since they comprised a tendency toward higher hardness and resistance to deformation, lower friction, and lower wear in the absence of oil.

Further development of methods of test for wear in the presence of lubricants may show that zinc tends to increase the weight losses and duration of the "wearing-in" period of bronze bearings, but since this is also a function of the perfection of fit such effects would be disadvantageous only in certain cases. The addition of 4 per cent zinc did not appreciably affect the wear rates subsequent to the "wearing-in" period.

In general, the results seem to justify the conclusion that the effects of zinc up to 4 per cent are generally small and may be insignificant in comparison with changes in properties quite readily produced in bronzes from variations in foundry practice. This should not be construed to apply to additions of zinc when other impurities are present.

VII. ACKNOWLEDGMENTS

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CRITICAL STUDY OF METHODS OF MEASURING THE BULK OF PAPER

By F. T. Carson

ABSTRACT

Because of the prevalence in the paper industry of diverse methods of measuring the property of bulk or voluminousness of paper, a study has been made of methods commonly used, and as a result of this investigation a standard method is proposed for measuring bulk. It was found that the different pressures used in the variable-pressure type of apparatus, and the use of an insufficient number of sheets in the case of measurements with thickness gages, are chiefly responsible for the diversity of results ordinarily obtained. As a result of comparative tests made on different types of apparatus and at various pressures, it was found possible to select procedures for the two most commonly used measuring devices so as to bring them into substantial agreement with each other and with the bulk actually obtaining in bound volumes.

A standard procedure is recommended which permits either the measurement of a pack of paper 0.1 inch or more in thickness with a thickness gage of standard type, or the measurement of a 1-inch pack under a pressure of 5 lbs./in.^{2} by means of a pressure bulker. It is recommended that the results be expressed as (*a*) bulking thickness, or the thickness in hundredths of an inch of a 100-sheet pack; and (*b*) specific bulk, or the ratio of bulking thickness to the standard ream weight of the paper measured.

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I. INTRODUCTION

The property of paper known as bulk is one of those vaguely defined characteristics frequently encountered in the older, empiric industries which may have varied interpretations and means of measurement. Because of the lack of any recognized standard procedure for the evaluation of this property, the Bureau of Standards, in cooperation with the Technical Association of the Pulp and Paper Industry in their program of standardizing paper-testing methods, has recently made a study of the measurement of the bulk of paper.

According to the varied usage of the term in the paper industry, bulk may mean (*a*) the thickness of a certain number of sheets, (*b*) the number of sheets in a 1-inch pack, (*c*) the thickness of a single sheet, (*d*) the ratio of thickness to ream weight, (*e*) specific volume, (*f*) the ratio of apparent volume to fiber volume. But in any discussion of bulk there is usually the idea, expressed or implied, of something equivalent to or proportional to specific volume. Bulkiness is thought of in terms of the thickness which a sheet of a given area can be made to have with a given amount of paper-making material. It is the antithesis of denseness or compactness.

The measurement of bulk is of importance chiefly to publishers and bookbinders and to the manufacturers who contract to supply paper to these converters. Because it is customary to prepare the bindings for books while the pages are being printed, it is necessary to know beforehand how thick a book is going to be. At one extreme, a premium is placed upon bulky paper, as, for example, in popular novels which are usually desired to be as thick as possible for a given weight of material. At the opposite extreme, paper having a low bulk is a desideratum, as, for example, in dictionaries and encyclopedias.

II. METHODS OF MEASUREMENT

According to the methods in common use for determining bulk the principal measurement is that of thickness made on one or more sheets. In practice this measurement may be made on any amount of paper, varying from a single sheet to a pack several inches thick. The paper is compressed more or less during the measurement, but there is little uniformity with respect to the pressures customarily used. The weight of the paper may or may not be taken into consideration, depending upon requirements and upon individual practice

The thickness measurement is often made with an ordinary rule held against the edge of a pack of paper which is pressed down with the hand. A sliding caliper or combination square is often used. Sometimes the measurement is merely the thickness of a single sheet determined by means of a micrometer caliper or other type

of thickness gage, or it may be the thickness of several sheets taken together. Sometimes the measurement is made after compressing the paper in a definite manner, such as by subjecting it to the pressure of a metallic disk of definite weight and cross-sectional area. But apparently only one instrument has been made specifically for the purpose of measuring bulk, the so-called pressure bulker.

III. STUDY OF METHODS OF MEASURING BULK

In an investigation with the object of selecting and recommending a standardized procedure it did not seem worth while to consider the procedures involving hand-rule measurements under indefinite hand pressures, since these pressures are not reproducible. After some preliminary study of different procedures three were selected for study and comparison. These are (*a*) measurement with the pressure bulker, (*b*) measurement by means of thickness gages, (*c*) measurement of the thickness of a pack of paper under pressure uniformly distributed over the entire pack.

1. PRESSURE BULKER

In this apparatus, which is illustrated in Figure 1, a pack of paper is clamped between two horizontal surfaces, the movable one of which communicates with a spring pressure gauge which indicates, in pounds per square inch, the pressure which is applied to the pack of paper. The surfaces are circular in form and have an area of 3 square inches each. A pointer attached to the movable pressure foot indicates on a vertical scale the distance between the two horizontal surfaces, which distance is the thickness of the pack. The scale supplied with the instrument is graduated in inches, and the smallest subdivisions are thirty-seconds of an inch. Pressure is applied by means of a screw jack turned with a hand wheel. The bulker is capable of exerting an indicated pressure of 50 lbs./in.^{2}, and can accommodate a pack of paper of any thickness up to 4 inches.

It was found in the instrument under examination that the guide stem of the pressure foot did not work freely. Its movement was very sluggish, and the pressure gauge did not respond readily to the pressures applied. The interior of the casting was found to be covered with molder's sand, some of which had become mixed with the lubricant and had given rise to considerable friction. After the interior and the moving parts had been thoroughly cleaned and the mechanism had been oiled the friction was greatly reduced, although an appreciable amount was still in evidence.

The pressure gauge was calibrated in an Amsler machine of 600 pounds capacity, a compression tester of the inclined balance type. The gauge was removed from the bulk tester and calibrated in its

normal upright position. It was necessary, therefore, to add the weight of the gauge to the applied pressure in each case in order to get the total pressure exerted by the pressure foot on the surface underneath it. The actual pressure, in pounds per square inch, exerted by the pressure foot for each calibrated-scale division was found by dividing this total pressure by three, the area in square inches of the pressure foot. It was found that with increasing load the actual pressure differed from the nominal pressure by amounts ranging from 1 to 5 per cent. The differences were not consistently positive or negative throughout, although for the higher pressures the actual pressures were greater than the nominal pressures. The differences between actual pressures exerted when using increasing load and when using decreasing load amounted in some cases to as much as 25 per cent for the lower gauge readings, although for the most part these differences, which are indicative of friction in the mechanism, did not exceed 5 per cent.

The bulk tester was fitted with a scale graduated in hundredths of an inch instead of the less-convenient scale supplied with the tester. It was then studied in operation in order to determine the effect upon the bulk test of a number of factors, such as the size of the sheets of paper, the thickness of the pack measured, the amount of pressure applied, the duration of the pressure, and the size of the pressure surfaces.

(*a*) Effect of Size of Sheets.—When a given pressure is applied to a given area of a pack of paper, the marginal portion of the pack outside of the direct influence of the pressure surface adds a certain resistance to that which the paper directly beneath the pressure surface offers to compression. It seemed that the size of this marginal area might influence the degree of compression of the pack. Since the greatest influence of this nature is to be expected from the most compressible paper, a sample of newsprint, which was the most compressible paper studied, was cut into two packs 4 by 5 inches and 8 by 10 inches, respectively, and tested for thickness under different pressures. The 8 by 10 pack appeared to be slightly thicker at a given pressure. This test, however, did not seem conclusive in view of the fact that the individual sheets of paper differ somewhat in thickness in a given sample. The 8 by 10 pack was, therefore, measured for thickness and was then cut into 4 by 5 packs which were again measured in the same places as before and under the same pressures, ranging from 0.5 to 40 lbs./in.^{2}. The two sets of readings, recorded to the nearest hundredth of an inch, were identical. Since the readings on the 4 by 5 pack were taken after those on the 8 by 10 pack, any influence which previous pressure might have on the measured thickness of the smaller pack would tend to exaggerate the difference, if any, between the two sets of measurements. But

as no differences were found in the two sets of readings in the latter test, it seemed valid to conclude that sheet size greater than about 4 or 5 inches square has no appreciable effect on bulk measurements as made by the pressure bulker. This conclusion was confirmed by tests in which a dial-thickness gage was attached to the bulker so as to permit of readings to thousandths of an inch. It was found that at a given pressure the thickness of a pack 8 inches square exceeded that of a pack 4 inches square by about 0.1 per cent for pressures ranging from 5 to 50 lbs./in.^{2}. This difference could not be detected in the ordinary use of the bulk tester.

(*b*) Effect of Size of Pressure Surfaces.—This effect is not unlike that due to sheet size. By increasing the size of the pressure surface the marginal area for a pack of given area is decreased. Measurements were made on a 4 by 5 inch pack of newsprint with pressure surfaces of 1, 3, and 5 square inches in area and for pressures ranging from 0.5 to 40 lbs./in.^{2}. The thickness data, recorded to the nearest hundredth of an inch, showed no appreciable differences for the three surfaces for a given pressure per unit surface. Measurements made to thousandths of an inch by means of the dial gage showed that for a given pressure per unit surface the thickness of a pack of book paper between surfaces 1 square inch in area exceeded that between surfaces 5 square inches in area by less than 0.2 per cent.

(*c*) Effect of Thickness of Pack.—It is usually considered that an accuracy of about 10 per cent in bulk standards and specifications is sufficient. Hence, it seems desirable that the measurement be accurate to within at least 1 per cent. For this reason the pack to be measured should be not less than about 1 inch in thickness when the scale graduated in hundredths of an inch is used and should be somewhat thicker for measurement with the scale permitting readings estimated to the nearest sixty-fourth of an inch. The necessary thickness of the pack is largely determined by the degree of refinement in the thickness measurement. When the dial gage was used, permitting readings to thousandths of an inch, readings could be repeated fairly consistently on packs which were thicker than about 0.05 inch, the concordance being better the thicker the packs. The use of a thick pack also affords a better chance of obtaining a fair sample.

(*d*) Effect of Pressure.—The most important variable in bulk measurements is the pressure applied to the pack while the thickness measurement is being made. The thickness varies considerably according to the pressure applied, and the effect is different for different kinds of paper. The relation between thickness and pressure is not linear. A given pressure change in the lower pressure region has a greater effect on thickness than does an equivalent pressure change

in the higher pressure region. Some typical data are presented in Figure 2 to show the effect on bulk measurement of different pressures and different kinds of paper, a pack of 250 sheets being used in each case.

Repeated applications of pressure within the capacity of the bulker did not materially alter the bulk at a given pressure. For example, a pack of the most compressible paper studied was ten

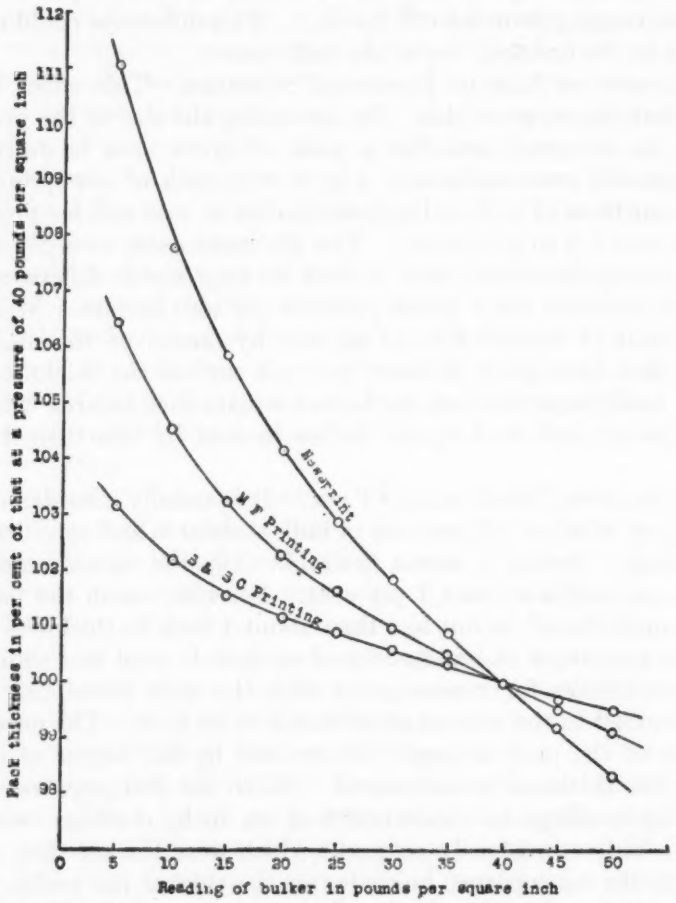

FIGURE 2.—*Effect of pressure and type of paper on bulk measurements*

times subjected to a pressure of 40 lbs./in.^{2} and was found to have lost only 1 per cent of its original thickness at a given pressure. After standing for some time, much of this was recovered. Various tests on different kinds of papers showed that little or none of the thickness is permanently lost by repeated applications of pressures within the capacity of the bulker. It was found that when a small loss appeared to have occurred it could virtually all be restored by

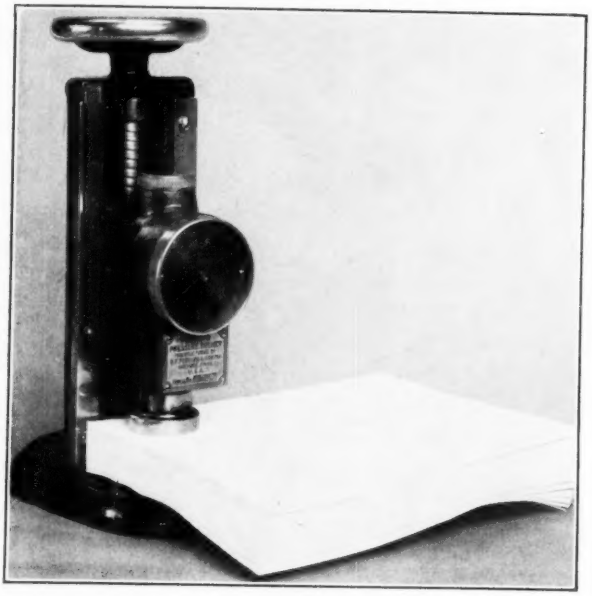

FIGURE 1.—*Pressure bulker*

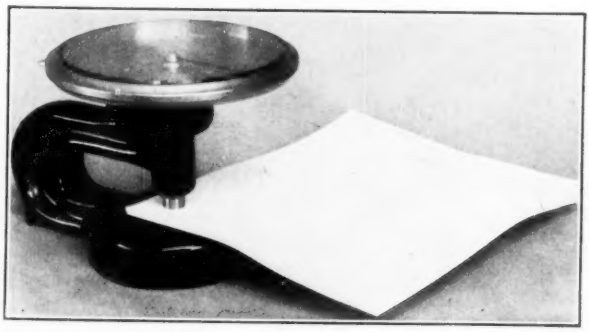

FIGURE 3.—*Thickness gage*

allowing the pack to stand for an hour or so or by flexing and thumbing the pack. Hence, it is evident that the deformation in machine-finished paper resulting from pressures not greater than about 50 lbs./in.^{2} is almost completely elastic. This is not so surprising when it is considered that such papers have previously been subjected to extremely heavy pressure in the calenders during their manufacture, so that the relatively much smaller pressures used in the bulk test have little or no permanent effect upon the papers.

Bulk measurements were made on paper under a pressure of 5 lbs./in.^{2} after having previously subjected the pack to a higher pressure. The test was repeated many times, using various higher pressures to precede the 5-pound pressure. In one series of tests the thickness showed a uniform, slight decrease regardless of the amount of pressure used to precede the 5-pound pressure. The test was repeated, but this time the paper was flexed between each set of measurements so as to enable the pack to recover the temporary decrease in thickness, and pressures from 10 to 50 lbs./in.^{2} were used to precede the 5-pound pressure. The bulk measurements all agreed to within about one-half of 1 per cent.

Tests were made to determine the effect of varying periods of time of application of pressure and of time intervals between operations. Time intervals of 10 to 30 seconds were used, and pressures of 5, 40, 0, and 5 lbs./in.^{2} were applied in sequence. The bulk measurements at a given pressure were in all cases the same. If time intervals of several minutes were allowed, differences might be noted, as is to be surmised from the fact that the small temporary decrease in thickness following the release of pressure is largely recovered within an hour or so. But in the normal, continuous procedure of bulk testing the rate of testing is not a factor in the results.

It appears, therefore, that the important requirements in the use of the pressure bulker are the adoption of a definite pressure at which all bulk measurements are to be made, the calibration of the pressure gauge in this pressure region, and the adoption of a pack thickness sufficient to give the required accuracy in the thickness measurements.

2. THICKNESS GAGES

A very common means of estimating the bulk of paper is to measure the thickness of a single sheet or a few sheets with some form of micrometer or thickness gage and then to calculate from this value the number of pages per inch or the thickness of a pack consisting of a large number of sheets. Since the thickness of the usual sheet of paper is of the order of 0.005 inch, it is apparent that measurements made with a micrometer graduated in thousandths of an inch may involve considerable differences when magnified manyfold by such a

calculation as the above. The percentage error would certainly be greater than the 1 per cent which appears to be the maximum error desirable in bulk measurements. Owing to the probability of a packing effect in an aggregation of sheets, or the fitting of excrescences of one sheet into depressions of another, it seemed doubtful if measurements made on single sheets would total to the same value as a single measurement made on all the sheets at once, even though equal accuracy of measurement were possible in the two cases. This packing effect, if real, would be an important factor in bulk measurement as opposed to thickness measurement on single sheets. Since the pressures exerted by different kinds of thickness gages differ considerably, it seemed possible also that the factor of pressure might influence the results of bulk measurements made by means of thickness gages. In order to determine the rôle of such factors a study was made of this mode of bulk measurement.

(*a*) Pressure of Thickness Gages.—Two micrometer calipers with ratchet heads, such as are used by machinists, were tested for the pressure exerted by the spindle on the material measured. One end of a lever pivoted at the center was allowed to rest against the end of the spindle and the other end was weighted until the friction on the spindle was sufficient to cause the ratchet to operate. With a smooth brass surface in contact with the spindle one micrometer was found to exert a pressure of about 33 lbs./in.^{2} and the other about 27 lbs./in.^{2}. But with a piece of blotting paper in contact with the spindle the pressure exerted was only about two-thirds as much as for the brass surface. The arresting of the rotation of the spindle depends not only upon the pressure against the spindle, but also on the coefficient of friction between the spindle and the material being measured. Hence, the pressure is different for different kinds of material calipered. For paper the pressure exerted by the spindle of this type of micrometer is in the neighborhood of 20 lbs./in.^{2}.

A dial micrometer (fig. 3) of a type conforming to the specifications of the Technical Association of the Pulp and Paper Industry was next examined and found to exert a pressure of about 10 lbs./in.^{2} on the material being measured.

A pack of newsprint paper about 0.2 inch thick was calipered by means of the dial micrometer and also by means of one of the ratchet-type micrometers, the latter exerting about twice the pressure per unit surface as the former. The thickness values obtained with the ratchet-type, rotating-spindle micrometer were between 1 and 2 per cent smaller than those obtained with the dial micrometer. This appears to indicate a much smaller influence due to pressure than was found for the bulk tester, a circumstance which is probably to be explained by the much smaller total pressures exerted by the thickness gages and the influence of the marginal area of the pack in leveling out the differences

which might otherwise exist in making measurements with thickness gages.

(*b*) MEASUREMENT ON SINGLE SHEETS AND ON A PACK OF PAPER.—Three sets of measurements were made on 11 different kinds of paper, each consisting of about 20 sheets. The papers were first exposed for at least an hour in the atmosphere where the tests were to be made, after which thickness measurements were made both on the individual sheets and on the entire pack at once. All measurements on each kind of paper were made at the same place on the sheets. One measurement was made on the pack before and another after the individual sheets were calipered, and these two measurements were averaged and compared to the sum of the measurements for the individual sheets. The results were then expressed as the percentage amount by which the sum of the single-sheet measurements differed from the pack thickness. These results are shown in the first three columns of Table 1. The differences range from less than one-half of 1 per cent to more than 7 per cent. Considering the individual measurements made on single sheets, it was found that errors as great as 17 per cent could result in bulk values determined from measurement of a single sheet. Thickness gages available are not sensitive enough for very accurate measurements on single sheets of paper, as a consequence of which errors of measurement on single sheets make it uncertain how significant are the differences noted in the table. But the fact that all these differences are of the same sign is interpreted to mean that the packing effect is real and of some importance in the measurement of bulk.

TABLE 1.—*Measurements with thickness gage*

Kind of paper	Difference between sum of single sheets and pack thickness			Reproducibility at 65 R. H.[1]		Humidity effect, 65 R. H. to 30 R. H.	
	65 R. H.	65 R. H.	30 R. H.	Pack	Single sheets	Pack	Single sheets
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Writing	+1.6	+1.1	+3.9	−0.1	−0.4	−1.6	+0.7
Bond	+3.0	+3.0	+2.4	−.1	−.1	−1.4	−1.9
Ledger	+1.2	+2.5	+3.3	+1.2	+2.5	−1.3	+.8
Coated book	+1.4	+1.8	+1.9	+.4	+.7	−1.3	−.7
S. and S. C. book	+1.2	+3.0	+3.4	+.4	+2.3	−2.4	−.2
Offset book	+3.5	+2.8	+3.4	+.1	−.6	−.8	−.8
Antique book	+2.4	+3.7	+2.9	+.1	+1.5	−1.0	−.5
"Hibulk" book	+3.3	+4.2	+3.6	−.1	+.7	−1.1	−.9
Mimeograph	+4.7	+5.7	+5.7	+.1	+1.0	−.7	+.3
Standard newsprint	+.4	+2.0	+3.2	+.6	+2.3	−2.0	+.5
Bulky newsprint	+6.6	+7.6	+7.5	+.5	+1.4	−.4	+.4

[1] R. H.=per cent relative humidity.

These data are also tabulated in columns 4 and 5 of Table 1 so as to show the precision which may be expected in the case of the two

procedures. These values represent the percentage differences in duplicate determinations. The agreement of duplicate determinations is much better for measurements on a pack of paper than for measurements on single sheets. Except for the ledger, the agreement is very good for measurements on the pack. The difference in the case of the ledger is probably real, rather than in the nature of an error of measurement, since the time allowed for conditioning was probably too short for such heavy paper.

The above observations relative to the packing effect and to the precision of measurement show that the current practice of calculating bulk from thickness measurements on a single sheet of paper should be discouraged, and that bulk measurements should always be made on a pack of paper of a thickness commensurate with the sensitivity of the measuring device.

(*c*) Effect of Humidity in Bulk Measurement.—In the last two columns of Table 1 are presented the percentage differences in the thickness of paper at 65 per cent relative humidity and at 30 per cent relative humidity, as determined both on the packs and on the individual sheets.

The data are expressed as the percentage change in thickness when paper is brought from moisture equilibrium at 65 per cent relative humidity to equilibrium at 30 per cent relative humidity. The results for measurements on single sheets show positive and negative differences about equally divided and confirm previous data to the effect that the influence of humidity changes in this region is of the same order of magnitude as the error of measurement of a single sheet of paper with a micrometer, and that it is, therefore, impossible to determine with certainty by the measurement of a single sheet of paper whether or not its thickness is altered by a change in moisture content. But the data obtained on packs of paper show a consistent decrease in all cases and indicate that the thickness of paper does change according to moisture content. About 2.5 per cent is the greatest difference shown by these data, but additional tests showed that in going from 65 to 15 per cent relative humidity thickness was decreased as much as 8 per cent in the case of one sample of paper.

3. BULKING PRESS TO APPLY UNIFORMLY DISTRIBUTED PRESSURE

The average pressure on the leaves of an ordinary book as it lies on the table is but a fraction of an ounce per square inch. On the other hand, during the binding process the book may have been subjected to pressures of 40 or 50 lbs./in.^{2}. In order to simulate to some extent these actual and extreme conditions met with in the life history of a bound volume so as to have a logical basis of comparison for bulk data, a bulking press was improvised by means of which such extremes of pressure, distributed uniformly over the

entire pack, could be applied. This apparatus is shown schematically in Figure 4. The pack of paper, P, was placed on a horizontal surface, S, and a thick aluminum plate, A, was laid on top of the pack. A dial gage, G, was provided for measuring the thickness of the pack at any time. The heavy pressures were applied by means of the lever, L, and a suitable weight, W_1. In applying the small pressures the lever was removed, a tripod, T, was placed on the aluminum plate so as to clear the gage, and a suitable weight, W_2, was added so that the combined load of this weight, the aluminum plate, the tripod, and the gauge pressure would produce the required pressure.

No especial refinements were deemed necessary in applying the heavier pressures, since these were intended primarily to approximate bookbinding pressures, and since, in the study of the pressure bulker, it was found that the amount of pressure preceding a bulk measurement at a comparatively light pressure might vary considerably without affecting appreciably this bulk measurement. However,

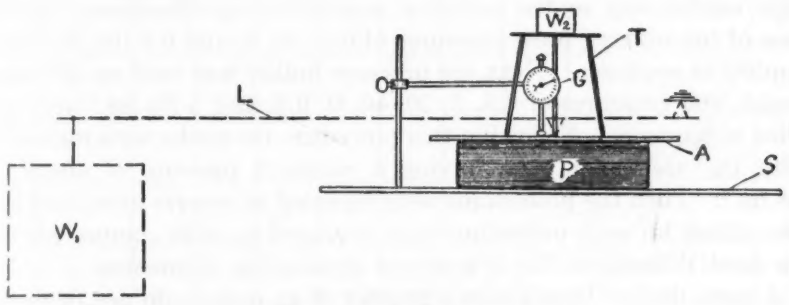

FIGURE 4.—*Bulking press*

the member serving as a knife-edge in contact with the plate, A, was made to extend entirely across the plate in the longer direction of the pack of paper, and both this member and the plate were of sufficiently sturdy construction to insure against appreciable warping of the plate under the heaviest pressures used. All reasonable care was taken to insure that the pressures actually applied through the lever system were approximately those desired in each case.

It was found impracticable to use the extremely low pressures of less than an ounce per square inch, as it was necessary to apply a few ounces per square inch to some of the papers in order to flatten them out sufficiently to give comparable results with the others. A working range of pressures having a minimum of about half a pound and a maximum of about 40 lbs./in.^{2} was found feasible for bulk measurements.

Experiments at pressures of a few ounces per square inch showed that the change in thickness per unit change in pressure in this low-pressure region is several times that which takes place in the

neighborhood of 5 lbs./in.^{2}, as is to be surmised from the shape of the curves of Figure 2. Because of this fact there is a certain disadvantage in working at very low pressures, since a greater degree of precision in applying the pressures is required in the low-pressure region. On the other hand, high pressures are much less significant in bulk measurements, since the thickness of a bound volume in use is determined by relatively small pressures.

The bulking press was further studied in connection with the pressure bulker and the thickness gage, using various pressures in measuring the bulking properties of several kinds of paper.

IV. COMPARATIVE TESTS BY THREE METHODS

Eleven kinds of paper, selected to represent the most important types in which bulk is a significant factor, were used for these tests. A pack of each, approximately 1 inch in thickness, was tested by means of the bulking press, the pressure bulker, and the thickness gage conforming to the technical association specifications. In the case of the bulking press pressures of 0.5, 40, 0, and 0.5 lbs./in.^{2} were applied in sequence. Next the pressure bulker was used on the same packs, and pressures of 0.5, 5, 20, 40, 0, 0.5, and 5 lbs./in.^{2} were applied in sequence. Following this procedure the packs were measured with the thickness gage having a constant pressure of about 10 lbs./in.^{2}. Then the procedures were repeated in reverse order, and the two values for each procedure were averaged so as to compensate for the small differences due to repeated application of pressure.

A pack thicker than about a quarter of an inch could not be measured with the thickness gage, so each pack was divided into four parts which were measured separately and the sum taken for comparison with the other methods.

It was necessary to modify the pressure bulker in order to get data at a pressure of 0.5 lb./in.^{2}. Such data were desired in order to determine the feasibility of a design of apparatus having the comparatively large pressure surfaces of the bulker, but dispensing with the screw jack and pressure gauge and using a constant low pressure in conjunction with a means of measuring the thickness of the pack. The pressure bulker was not designed for recording such low pressures, but the required pressure was obtained by taking off the cap screw and weighting the pressure foot by the required amount. It was necessary also to take into consideration the friction in the guide stem, since it was too great to be neglected in this low-pressure region. The pressure was measured, as in the case of the thickness gages, by means of a weighted lever.

TABLE 2.—*Comparative tests*

Kind of paper	Identification	Ream weight, 25 by 40–500	Thickness of 100 sheets (in hundredths of an inch)											
			Bulking press 40–0–0.5	Bulker modified, 40–0–0.5	Bulking press, 0.5	Bulker modified, 0.5	Pressure bulker, 40–0–5	Pressure bulker, 5	Bulking press, 5	Thickness gauge	Pressure bulker, 20	Pressure bulker, 40	Bulking press, 40	Specific bulk [1]
		Lbs.												
Writing	W	51	35.6	35.6	35.9	35.9	34.4	34.8	34.4	34.6	34.1	33.3	33.4	0.68
Bond	B	65	47.0	47.5	47.5	48.0	46.0	46.0	46.0	45.8	45.0	44.0	44.5	.70
Ledger	L	97	58.7	58.7	58.7	59.3	56.9	56.9	56.9	56.6	56.2	55.6	55.6	.58
Coated book	C	83	40.6	41.1	41.1	41.1	39.4	39.4	39.4	39.4	38.9	38.9	38.9	.47
S. and S. C., book	S	53	31.6	31.3	31.6	31.6	30.6	30.6	30.3	30.4	30.0	29.6	29.6	.57
Offset, book	O	58	52.2	52.2	53.3	52.8	50.6	51.1	50.0	50.6	49.4	48.9	47.8	.87
Antique book	A	54	51.1	51.7	52.2	52.2	50.0	50.0	50.0	50.0	48.9	47.8	48.3	.93
"Hibulk" book	H	56	67.8	67.8	69.3	69.3	65.0	65.7	65.0	65.5	63.6	62.1	60.7	1.17
Mimeograph	M	51	47.5	48.0	49.0	48.5	46.0	46.5	46.0	46.2	45.0	44.0	44.0	.91
Standard newsprint	N	37	37.2	37.6	37.6	37.6	35.2	35.6	36.0	35.4	34.0	32.8	32.8	.96
Bulky newsprint	K	37	52.2	52.2	53.9	53.3	48.3	48.9	47.8	48.2	46.1	44.4	43.9	1.30

[1] Calculated from measurements with thickness gage.

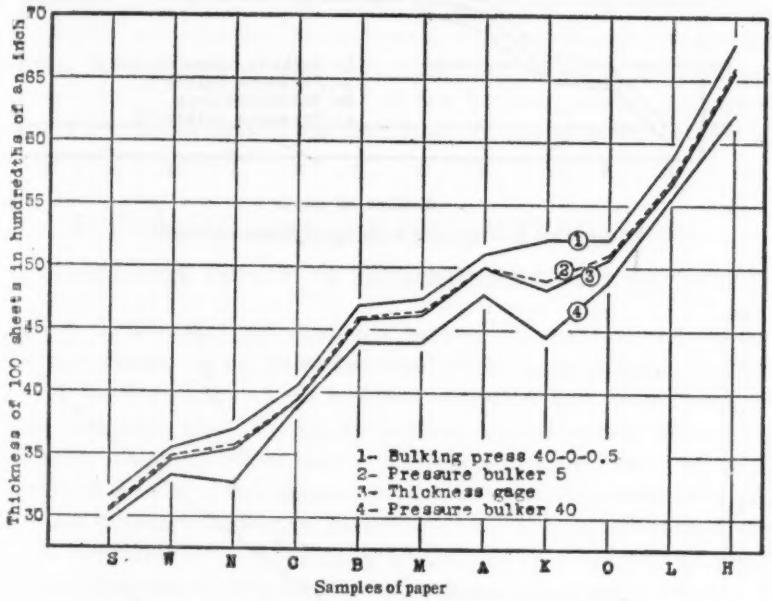

FIGURE 5.—*Bulking thickness by different methods*

The results of these comparative tests are shown in Table 2 and in Figures 5, 6, and 7. In the table the results are expressed as bulking thickness, or the thickness in hundredths of an inch of a pack of paper consisting of 100 sheets. The pressure applied for each procedure is noted in the heading for that column. For example, the results in the third column, headed "Bulking press, 40–0–0.5," were obtained by applying a pressure of 40 lbs./in.^{2} by means of the bulking press, entirely releasing this pressure, and then applying a pressure of 0.5

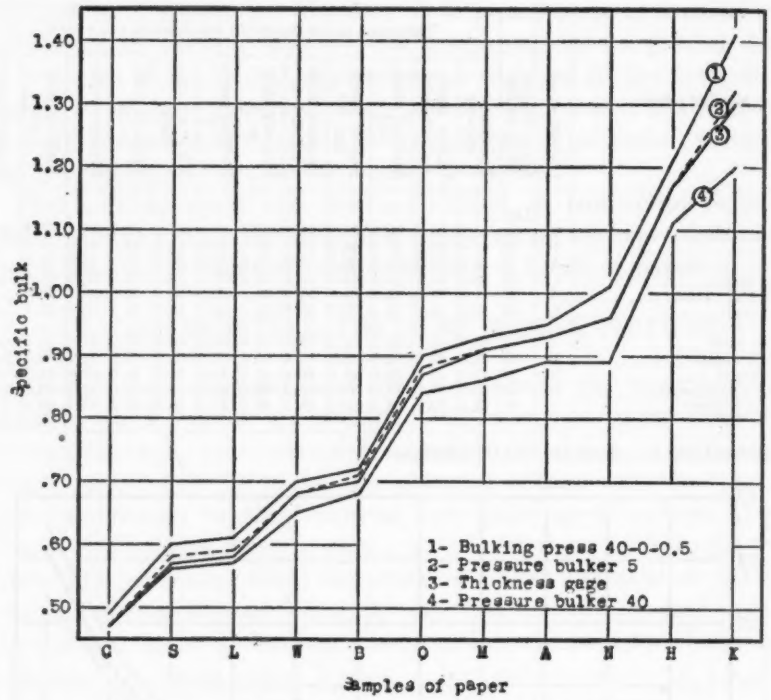

FIGURE 6.—*Specific bulk by different methods*

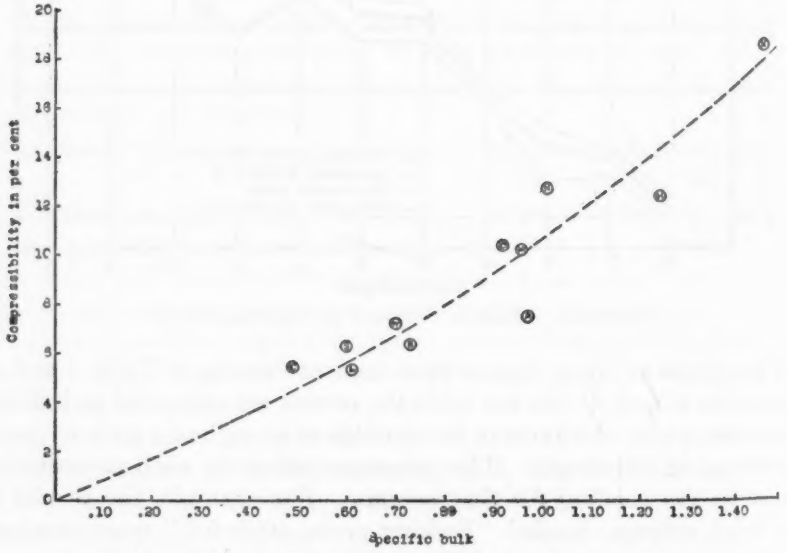

FIGURE 7.—*Relation of compressibility to specific bulk*

lb./in.^{2}, immediately after which the thickness of the pack was determined. The weight in pounds of the standard ream of 500 sheets, 25 by 40 inches in area, is given for each kind of paper, as this quantity is required in calculating the specific bulk. An identification symbol is given each kind of paper as a matter of convenience in making the graphic tabulations of Figures 5 and 6. In these graphs the samples of paper tested are the abscissas, and the values for the quantity determined on each are plotted as ordinates. In Figure 5 the data of Table 2 are plotted for four different procedures in the increasing order of bulking thickness as determined by the procedure first tabulated. In Figure 6 the data, expressed as specific bulk, are plotted in the increasing order of bulk. Specific bulk is proportional to specific volume of the packs and is the ratio of bulking thickness to ream weight. Specific bulk values for the different papers are shown in the last column of Table 2. The relation between specific bulk and compressibility is shown in Figure 7, from which it is seen that they are roughly proportional, as might be expected. Since thickness is not directly proportional to pressure, compressibility is arbitrarily taken as the per cent change in pack thickness when the pressure is increased from 0.5 to 40 lbs./in.^{2} in the bulking press. The specific bulk in this case is that at the beginning of the same procedure, at a pressure of 0.5 lb./in.^{2}.

V. CONCLUSIONS AND RECOMMENDATIONS

1. NEGLIGIBLE EFFECT OF PRELIMINARY HEAVY PRESSURE

At first it was thought that any method of measuring bulk to be really significant would have to simulate to some extent the conditions of bookbinding which involve rather heavy pressures, as it seemed probable that the heavy pressures used would have an appreciable permanent effect on the thickness of a volume. It was for this reason that in a preliminary report it was recommended that in using the pressure bulker a pressure of 40 lbs./in.^{2} should first be applied, then released, and finally a pressure of 5 lbs./in.^{2} be applied and the thickness measurement made under this lower pressure. It was for this reason also that the procedure with the bulking press which has been adopted as the reference basis for this series of comparative tests includes a pressure of 40 lbs./in.^{2} to precede the light pressure of 0.5 lb./in.^{2} under which the thickness measurement is made. But the data in Table 2 indicate that the results at any given pressure are pretty much the same regardless of whether or not a heavier pressure has just preceded that at which the thickness measurement was made.

2. CHOICE OF METHOD

The bulking press, which simulates the conditions associated with a bound volume and which has been made the touchstone of the comparative tests herein reported, is not a practical solution of bulk measurement. It is a logical procedure and is excellent for measuring the bulk of a thick pack of paper in sheets of small size. But in practice there may be relatively few sheets and they may be of any size from a few square inches in area to a thousand or more. An apparatus having pressure surfaces a thousand square inches in area would be unwieldy, expensive, and awkward to use and would require means of applying a total load of not less than 500 pounds for a full-size ream of book paper. Such a large pressure foot could scarcely be made light enough or be readily counterbalanced for use with small sheets and small loads without introducing an undesirable amount of friction. The data of Table 2, taken with the modified bulker at a pressure of 0.5 lb./in.^{2}, indicate that an apparatus having pressure surfaces a few square inches in area and designed to exert a small pressure would probably be satisfactory for the measurement of bulk, especially of relatively thick packs of paper. But, despite the fact that existing instruments for bulk measurement are not ideal for the purpose, there are several reasons why it does not seem desirable to recommend the design of a new type of apparatus to displace them. Such an instrument would have to be rather precise and, therefore, expensive in order to give sufficiently accurate results on thin packs, a demand often met with in the practical measurement of bulk. Frequently when a manufacturer is called upon to match a sample of paper for bulk only a small sample has been submitted, and the necessary data must be obtained from a few small sheets. Furthermore, bulk is not usually considered a major property of paper, and the tolerances in the specification of bulk are rather liberal, so that if conditions of operation for existing apparatus can be found which will give consistent relative results approximately paralleling the bulk values for paper in bound volumes it seems preferable to standardize the operation of existing apparatus rather than to create a new type of testing device. In any practical solution of the problem of bulk measurement it appears that only relative values can be obtained anyway, as is indicated by the results with the bulking press which are themselves only relative, since the normal pressure to which a bound volume is subjected is usually less than the smallest pressure found practicable in using the bulking press.

That it is feasible to use existing instruments under certain conditions is indicated by the data shown graphically in Figures 5 and 6. The results of curve 3, which were obtained with a thickness gage of standard type, are on the average 97 per cent of the corresponding

values for curve 1 obtained with the bulking press, and in only one case do they deviate more than 1 per cent from this relative amount. This one exception, the bulky newsprint, is about 4 per cent lower than it should be to stand in the proper relation to the other values. It may be seen from Figures 6 and 7 that this paper is also singular in that it has the highest specific bulk and the greatest compressibility of all the samples tested. It appears from Figure 6 that the results at different pressures tend to diverge with increasing specific bulk and compressibility. (Fig. 7.) In general, therefore, it appears valid to determine relative bulk with the thickness gage, using a pack thick enough to be consistent with the sensitivity of the instrument, and possibly being a little more lenient with the tolerances in the case of very bulky, compressible paper.

As is indicated by curve 2 (figs. 5 and 6), the use of the pressure bulker at a pressure of 5 lbs./in.^{2} gives results which agree very closely with those obtained with the thickness gage. It happens that this pressure is a fair compromise between the rather high pressures often used in measuring bulk and the very low pressures which are, perhaps, most significant in connection with bulk. As the pressure is increased above this amount the parallelism becomes less and less satisfactory.

It appears, therefore, that not only is it possible to choose conditions of operation of existing devices which will give satisfactory relative results, but the proper choice of conditions brings the two most widely used instruments for bulk measurement into close agreement.

3. EXPRESSION OF RESULTS

Practice differs considerably with respect to the expression of results. Bulk is usually expressed in terms of thickness as a matter of convenience in connection with bookbinding. But some express the results as the number of pages to the inch and others as the thickness of a certain number of pages. The latter seems the more logical of the two, since increasing thickness for a given amount of material varies in the same direction as the concept of increasing bulk. An increasing number of pages to the inch, on the other hand, connotes decreasing bulk. An expression of the number of pages to the inch should be associated with compactness rather than with bulk.

As a result of the usual practice of expressing bulk data in terms of thickness the fundamental concept of bulk is often lost sight of. But primarily bulk is a specific property of paper akin to specific volume, although for the sake of convenience it is not usually so expressed. It seems logical and desirable to recognize two aspects of bulk, which are essentially usages (*a*) and (*d*) mentioned in the introduction, and to express the results in two ways: (*a*) As bulking thickness, to mean the thickness in hundredths of an inch of a 100-sheet pack of paper; and (*b*) as specific bulk, to mean the ratio of bulking

thickness to the weight in pounds of the standard ream of 500 sheets, 25 by 40 inches in area. Bulking thickness is then a convenient quantity in connection with bookbinding, and specific bulk is a quantity which expresses the inherent quality of the paper with respect to bulk and is so chosen that the usual book papers have a value in the neighborhood of unity. (See last column of Table 2.)

4. RECOMMENDED STANDARD PROCEDURE

A standard testing method and manner of expressing the results of bulk determinations are recommended as follows:

The bulk tests shall be carried out in an atmosphere of standard hygrometric state (65 per cent relative humidity and 70° F.) as prescribed by the Technical Association of the Pulp and Paper Industry, and the paper to be tested shall have been properly conditioned in this atmosphere. The pack thickness shall be measured by one of the following alternate procedures:

1. A dial thickness gage of a type conforming to the specifications of the Technical Association of the Pulp and Paper Industry [1] shall be used. A pack of paper not thinner than 0.1 inch shall be measured for thickness on the four corners by means of this gage, a margin of at least half an inch between the pressure foot and the edges of the pack being maintained during the measurement. The average of the four readings shall be used in calculating the bulk values.

2. A pressure bulker shall be used, having a pressure foot not less than 1 square inch in area and being provided with means of applying a definite known pressure of 5 lbs./in.^{2} and means of measuring the distance between the pressure surfaces. A pack of paper approximately 1 inch in thickness shall be measured at the four corners between the pressure surfaces of this bulker under a pressure of 5 lbs./in.^{2}, a margin of at least half an inch between the pressure foot and the edges of the pack being maintained during the measurement. The average of the four readings shall be used in calculating the bulk values.

In either case the results shall be expressed as—

(*a*) Bulking thickness = Thickness in hundredths of an inch of a 100-sheet pack,

(*b*) Specific bulk = $\dfrac{\text{Bulking thickness}}{\text{Weight of standard ream (25 by 40–500) in pounds}}$

WASHINGTON, July 10, 1928.

[1] Paper testing methods, p. 55; 1928.

SOME OBSERVATIONS OF SHORT-PERIOD RADIO FADING

By T. Parkinson

ABSTRACT

The data presented are the product of an investigation started at the beginning of 1928 with the object of studying the short-period fading of radio broadcast transmissions. Particular attention was paid to those intensity changes which take place during periods ranging from a few seconds to several minutes. Various antenna combinations were used in making simultaneous records in order to separate the effects of various causes of fading.

It was concluded that, in addition to the more commonly accepted causes, there may be a number of indirect rays with varying paths and with rotating planes of polarization which give rise to the variations in intensity of the received signal. Some of the conclusions are consistent with those of other workers in the field, but new explanations are necessary for some of the data.

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I. INTRODUCTION

The data presented in this paper are the product of an investigation started by the Bureau of Standards at the beginning of 1928 with the object of studying the short-period fading of radio broadcast transmissions. This study was directed particularly to those intensity changes in the receiving antenna which range, in period, from a few seconds to several minutes between peaks. These variations have been variously ascribed by previous investigators to one or more of the following causes: (1) Intensity changes undergone by the indirect or atmospheric ray, namely, that portion of the radiation which, at night especially, travels to the upper atmosphere and is returned to earth at the receiving antenna by refraction; (2) inter-

ference, due to varying phase relationships of two or more indirect rays or of an indirect ray and the ground ray, which follows a direct path along the surface of the earth from transmitting to receiving antenna; (3) direction shifts, this expression being used to connote deviations of the indirect ray from the great circle plane passing through transmitting and receiving points; (4) changes in the angle of incidence (that is, in the vertical plane of arrival of the indirect ray); (5) rotation of the plane of polarization of the atmospheric ray, this rotation being considered as a continuous process rather than in the optical sense of a definite displacement of the plane at completion of the process. The aim of the present investigation was to separate the effects due to the above-mentioned causes with a view to determining to what extent each might be a factor in fading.

II. METHOD AND APPARATUS

The method consisted in selecting a particular broadcasting station and making simultaneous graphic records of its carrier wave as received by different types of antennas attached to duplicate receiving sets. The antennas used were (1) a vertical single wire, 15 m high, with a 2 m horizontal lead-in; (2) a vertical coil having its turns in a great circle plane common to transmitting and receiving points, which coil will hereafter be referred to as "at maximum," or "in the maximum position"; (3) a vertical coil perpendicular to the great circle plane and hereafter to be designated as "at minimum," or "in the minimum position"; (4) a so-called barrage antenna, consisting of the single-wire antenna so coupled to a coil antenna in the maximum position as to introduce an out-of-phase current and thus neutralize the effect of the ground ray as well as of the vertical component of the indirect ray. The coil antennas were so balanced by a center-tap arrangement as to eliminate any appreciable "antenna effect." For all tests the various antennas were located from 3 to 5 m apart. These distances were sufficiently small so that records obtained simultaneously with similar antennas were alike, and were sufficiently large to prevent interaction between the separate receiving circuits. All observations were made at the Bureau of Standards field station located at Kensington, Md., 8 km north of the bureau and in a position practically free from "man-made" interference and distorting influences.

Other apparatus employed was essentially that described by G. W. Pickard[1] in 1923 and used later in the cooperative investigation conducted by the Bureau of Standards in 1925.[2] The receiving sets were superheterodynes of the same make and were capable of adjustment to practically the same amplification. The driving motors of

[1] G. W. Pickard, Short-period Variations in Radio Reception, Proc. Inst. Radio Eng., **12**, pp. 119-158; April, 1924.

[2] J. H. Dellinger, C. B. Jolliffe, and T. Parkinson, Cooperative Measurements of Radio Fading in 1925, B. S. Sci. Paper No. 561, pp. 423-425.

the Shaw manual recorders were automatically synchronized every second, thus making it possible to compare two records by superposition.

Observations were concentrated largely upon two stations, but less-frequent records were made on transmissions from other stations involving frequencies of 550 to 1,480 kc and direct-transmission paths of 13 to 1,500 km. The greater number of records were made upon WJZ, Boundbrook, N. J., and upon WBAL, Baltimore, Md., because of the regularity with which each could be received, day or night, and because of what appeared to be characteristic features. Many of the observations started during daylight when there was no appreciable indication of an indirect ray and when, consequently, the most accurate bearings could be secured with the coil antennas. At this time, also, the two receiving systems could be so adjusted that the ground wave produced the same deflection on the recorder galvanometers of the two receiving systems. When records were started after dark no attempt was made to have them on an accurately comparable intensity basis, the chief aim being to study the simultaneous changes on two records rather than their exact magnitudes.

The arrangement of the pairs of simultaneous records in the illustrations will be found somewhat inconsistent, since the character of the records made it easier to compare them by placing the one made with a given type of antenna sometimes above, sometimes below the record made with another type.

III. RESULTS

1. SIMULTANEOUS COIL AND VERTICAL SINGLE-WIRE ANTENNA RECORDS

The first method of analysis in the present investigation was by means of simultaneous fading records made with coil antenna in maximum position and with vertical single-wire antenna, respectively. Assuming both ground and reflected rays to be in the great circle plane which passes through transmitting and receiving points, certain effects were anticipated. The ground ray presumably remains normally polarized at night as during daylight; therefore, so long as there is a normally polarized component of the indirect ray any changes in the path length of the latter should result in changing phase relations between the two rays, and, consequently, in similar and simultaneous intensity variations in the two types of antenna. Since the total electric vector in the vertical plane is effective on the coil antenna, the signal strength in it should range between the sum and the difference of the two fields produced by direct and indirect rays, respectively. On the vertical single-wire antenna similar variations should be of less absolute magnitude, since only the vertical component of the electric vector is effective and this component decreases with

the angle of incidence. With either antenna the night intensity, for nonlocal stations at least, will sometimes exceed, sometimes fall below the relatively constant daylight level, and similar variations should occur simultaneously on both records.

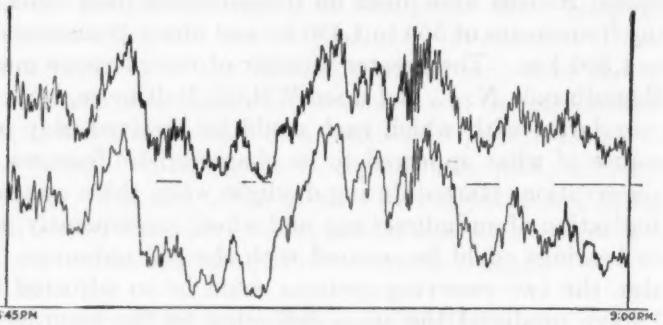

FIGURE 1.—*WIOD (1,210 kc), Miami Beach, Fla., received at Kensington, Md., 1,500 km, March 15, 1928*

Upper record with vertical single-wire antenna; lower record, coil antenna at maximum.

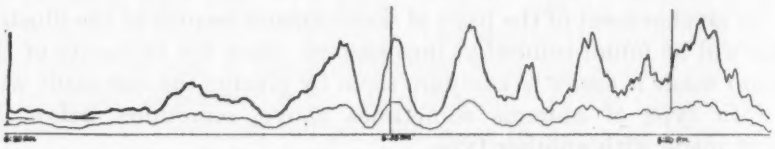

FIGURE 2.—*WJZ (660 kc), Boundbrook, N. J., received at Kensington, Md., 300 km, May 15, 1928*

Upper record, coil antenna at maximum; lower record, vertical single-wire antenna.

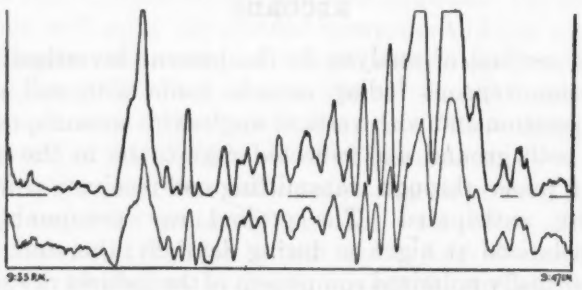

FIGURE 3.—*WRVA (1,180 kc), Richmond, Va., received at Kensington, Md., 155 km, June 1, 1928*

Upper record, coil antenna at maximum; lower record, vertical single-wire antenna.

Turning now to the data and examining some 50 records involving transmission frequencies of 660 to 1,480 kc and distances of 13 to 1,500 km, what do we find? For stations more than about 150 km distant from the receiving antennas the results were practically as anticipated, as the typical graphic records of Figures 1 to 3 indicate.

There is a slight shifting of phase at one point in the WIOD record shown in Figure 1 which may be real or may have been caused by changing speed of one recording drum at a time when there was difficulty with the synchronization of the two drums. Conditions prevented making another record on this station. With this single exception the intensity changes are in phase on the two antennas. An anomaly appears, however, in the records for the nearer group of stations (13 to 53 km distant) in that the intensity changes are at times as much as 180° out of phase on the two records. This holds true for variations of a few seconds duration as well as for those having periods of a minute or two. Figures 4 to 7 show typical illustrations. Here we have the same effect that Appleton and Ratcliffe [3] found in

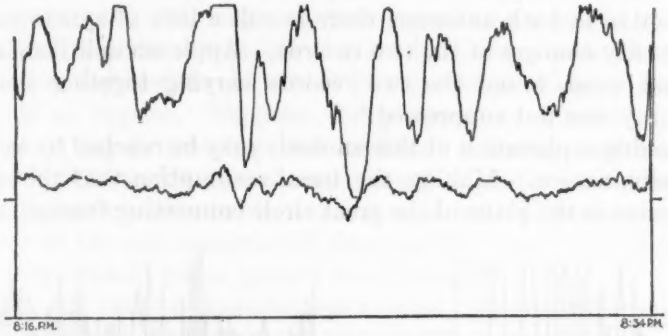

FIGURE 4.—*WBAL (1,050 kc), Baltimore, Md., received at Kensington, Md., 50 km, May 9, 1928*

Upper record, coil antenna at maximum; lower record, vertical single-wire antenna.

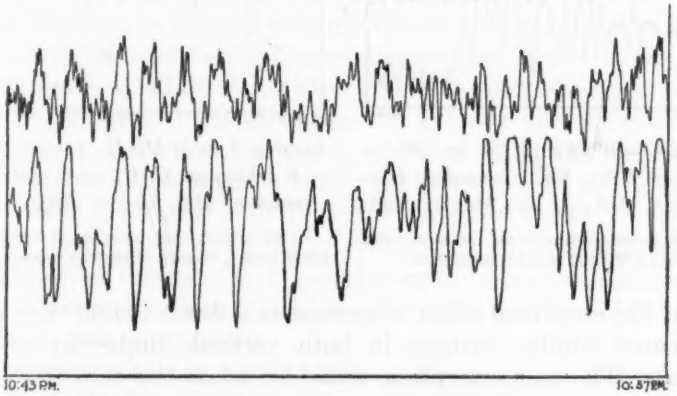

FIGURE 5.—*WTFF (1,480 kc), Mount Vernon Hills, Va., received at Kensington, Md., 31 km, March 19, 1928*

Upper record, vertical single-wire antenna; lower record, coil antenna at maximum.

[3] E. V. Appleton and J. A. Ratcliffe, On the Nature of Wireless Signal Variations, Proc. Royal Soc., **115A**, pp. 291-317; June, 1927. See especially pp. 311-312 and fig. 9.

simultaneous records made with vertical single-wire antenna and with the ground ray suppressed in a single-turn loop placed in the maximum position. They accounted for the recorded differences by an interference between indirect and ground rays which was effective in the vertical antenna but was eliminated from the loop. This explanation is not applicable to the present data, since with the ground ray effective in both antennas there is still a lack of synchronism in the intensity changes of the two records. Appleton and Ratcliffe, on the other hand, found the two records varying together when the ground ray was not suppressed.[4]

A possible explanation of this anomaly may be reached by the process of elimination. Making the usual assumption that the indirect ray remains in the plane of the great circle connecting transmitter and

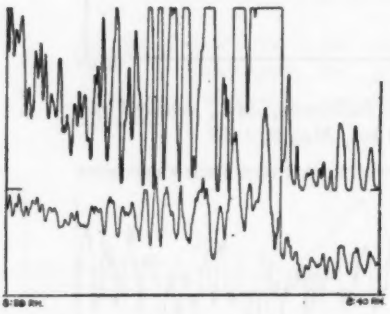

FIGURE 6.—*WTFF (1,480 kc), Mount Vernon Hills, Va., received at Kensington, Md., 31 km, May 17, 1928*

Upper record, coil antenna at maximum; lower record, vertical single-wire antenna.

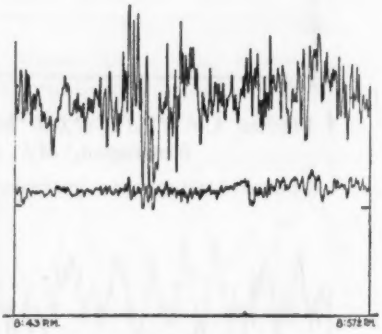

FIGURE 7.—*WMAL (1,240 kc), Washington, D. C., received at Kensington, Md., 13 km, May 7, 1928*

Upper record, coil antenna at maximum; lower record, vertical single-wire antenna.

receiver, the combined effect of ground and downcoming rays should be to cause similar changes in both vertical single-wire and coil antennas. The only exception would be when the atmospheric ray arrived with zero angle of incidence, in which case only the ground ray should be effective in the vertical antenna and the intensity should remain at the daylight level, while in the coil antenna the combined effect of the two rays should continue to produce fading changes. This explanation does not fit the data; it is a change of phase relationship between the two records, not a cessation of fading in one, that that is to be accounted for. Rotation of the plane of polarization of the incident ray also should produce like effects in the two receiving systems; therefore, by itself, this offers no solution.

The answer is presumably associated, directly or indirectly, with the nearness of transmitting and receiving stations. For the distances

[4] Reference 3, p. 300, figs. 4 and 5.

concerned, 13 to 53 km, it is perfectly possible to have direction shifts of the incident ray as great as 90°, due to irregularities in the refracting or reflecting upper atmosphere. This could account for changes on the vertical antenna not occurring on the coil antenna, but not for the considerable time lag between similar changes produced in the two receiving systems. If, however, there should be a lateral direction shift combined with a rotation of the plane of polarization for the downcoming ray, we should expect just such differences in the pairs of records as appear. Suppose, for purposes of illustration, that the reflected ray is arriving with constant intensity and normally polarized. If, now, the lateral angle of arrival shifts until it becomes 90°, the signal intensity in the vertical antenna will remain constant while that in the coil antenna will decrease to a minimum; in fact, to zero, if there should be no ground wave present.

If, next, the plane of polarization rotates, the vertical component of the electric field will decrease until, with the electric field horizontal, the ray ceases to produce a current in the vertical antenna. Simultaneously, the component of the magnetic field in the vertical plane will have increased from zero to a maximum, thereby producing maximum current in the coil antenna for the given angle of incidence. Thus we have similar fading characteristics 180° out of phase in the two antennas. If the direction of arrival of the incident ray gradually returns to the plane of the maximum coil antenna and the rotation of the plane of polarization continues, whether at regular or irregular speed, the phase difference between the two records will gradually decrease until it disappears. With the direction shifts more or less erratic we should have just the sort of changing phase relations shown on the records of Figures 4 to 7; and if rotation ceased, we should again find the two records running in phase, as in the early part of Figure 5 or the latter part of Figure 6.

The question whether the direction shifts necessary to the above explanation actually exist requires proof. Bearings on these stations were taken at night by means of a coil antenna and revealed apparent direction shifts which were considerable. An actual test, however, can only be made with an antenna of the Adcock type [5] if true directions of arrival of the reflected ray are to be found. Such a test awaits the construction of further apparatus.

Interference between the indirect ray and the ground ray is evidenced on many of the records made with the coil antenna in maximum position, and to a lesser degree by those made with the vertical single-wire antenna. Wherever the intensity of one of these records falls

[5] Improvement in means for determining the direction of a distant source of electromagnetic radiation. British Patent 130490, 1919. For actual applications, see reference 14 in appendix.

below the daylight level the indirect ray must be to some extent out of phase with the waves arriving along the surface of the earth. Figures 4 to 7 give clear indications of this. Note particularly that even for stations as near as 13 km from the observing point, as shown by Figure 7, the intensity of the downcoming ray is sometimes nearly as great as that of the ground wave, so that when the two are opposite in phase the intensity of the ground ray is largely neutralized and the record drops almost to zero. Presumably in these same records the peaks are due to the addition of the reception by direct and indirect paths. It will later be shown, however, that peaks may be due to other causes, whether the ground wave be present or not.

2. SIMULTANEOUS FADING RECORDS WITH TWO COIL ANTENNAS AT MAXIMUM AND MINIMUM POSITIONS, RESPECTIVELY

The second method of analysis was by simultaneous fading records of the same transmission as received by two coil antennas, one in the maximum and the other in the minimum position. The purpose of

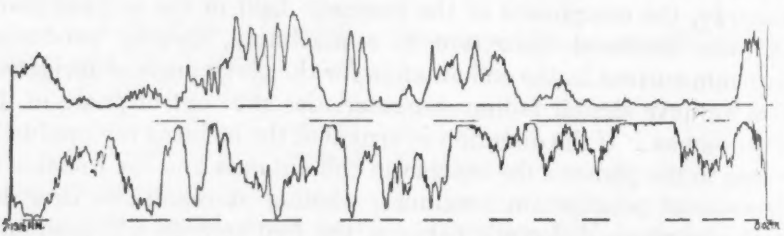

FIGURE 8.—*WJZ (660 kc), Boundbrook, N. J., received at Kensington, Md., 300 km, April 2, 1928*

Upper record, coil antenna at maximum; lower record, coil antenna at minimum position.

this arrangement was to secure some data as to fading caused by rotation of the plane of polarization of the indirect ray, for such a phenomenon, if present, should cause an increase of intensity in either coil antenna to be accompanied by a decrease in the other. So far as possible the minimum bearing was found for the various stations during daylight when there was no evidence of an indirect ray, and these bearings checked satisfactorily on different days. For the more distant stations, however, no ground wave could be received in daylight, and it was necessary to trust to approximate bearings, which were sufficient for the project in hand.

The data secured offers considerable striking evidence of the above-mentioned phenomenon. Figure 8 is a typical section cut from a pair of simultaneous records. Here it is possible to see at a glance that the two are practically 180° out of phase most of the time. The minima do not always fall to zero as would be expected with the ground wave practically negligible, as it is in this case, and it, therefore, becomes necessary to postulate more than one indirect ray.

It may be that in this record we have the effect of two rays rotating at different speeds so that their minima do not synchronize most of the time. Interference between the two is also probably present, but the effect can not be isolated in the record. Figure 9 is another record made on reception from the same station as Figure 8 and is typical of what occurs during the sunset period. Up until a half hour after sunset the weak ray from the upper atmosphere appears to remain normally polarized and so produces intensity changes only in the coil at maximum position, possibly through a combination of interference effects and varying absorption. Then gradually evidence appears that an indirect ray somewhat abnormally polarized is producing a current in the minimum coil. With no further rotation of the plane of polarization any variations in the intensity of the indirect ray may now result in parallel changes such as appear in the first large intensity peak at 7.12. Here, due probably to the combined effects of very abnormal polarization and of small angle of incidence

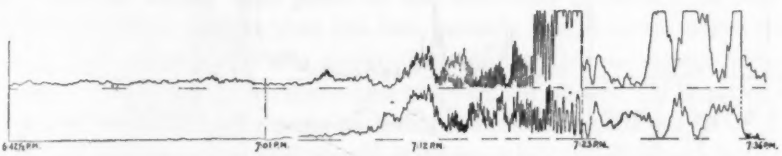

FIGURE 9.—*WJZ (660 kc), Boundbrook, N. J., received at Kensington, Md., 300 km, April 5, 1928*

Local sunset at 6.36. Upper record, coil antenna at maximum; lower record, coil antenna at minimum.

accompanying increased height of the ionized layer, the intensity in the coil at minimum is practically the same as in that at maximum. From this peak on, nearly to the end of the record, the average trend of the maximum coil antenna record is 180° out of phase with the minimum, indicating that the rotation of the plane of polarization of the indirect ray has gotten under way. Starting at about 7.04 p. m. on this same record there is a superposed rapid variation having a period of from 3 to 30 seconds. This characteristic is also exactly out of phase on the two records and so suggestive of a second and relatively much weaker ray with plane of polarization rotating rapidly. Assuming the polarization to be plane, a complete rotation would have to occur in six seconds to produce the most rapid of these changes.

While these data and much more seemed to be consistent with rotation of the plane of polarization in the indirect ray, there were times when the phase difference between the two records varied widely, sometimes becoming almost zero, as shown in Figures 10 to 12. The ground ray could in no way be held responsible, for its effect had been eliminated by the coil antenna in minimum position, and yet variations in one antenna led or lagged behind similar variations in the

other. In a recent article Eckersley[6] reports that records of high-frequency transmissions received simultaneously with vertical and

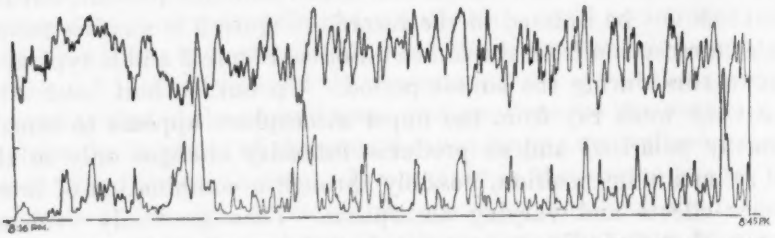

FIGURE 10.—*WBAL (1,050 kc), Baltimore, Md., received at Kensington, Md., 50 km, April 17, 1928*

Upper record, coil antenna at maximum; lower record, coil antenna at minimum.

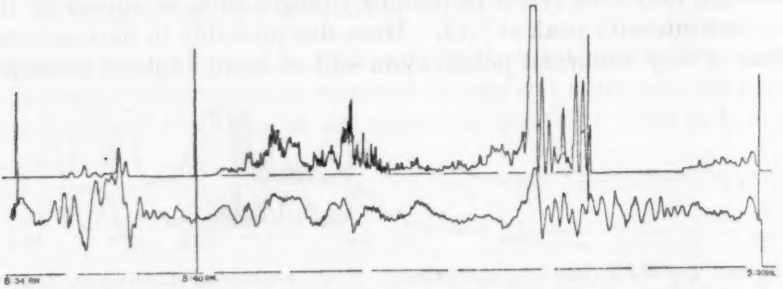

FIGURE 11.—*WMAL (1,240 kc), Washington, D. C., received at Kensington, Md., 13 km, June 5, 1928*

Upper record, coil antenna at minimum; lower record, coil antenna at maximum.

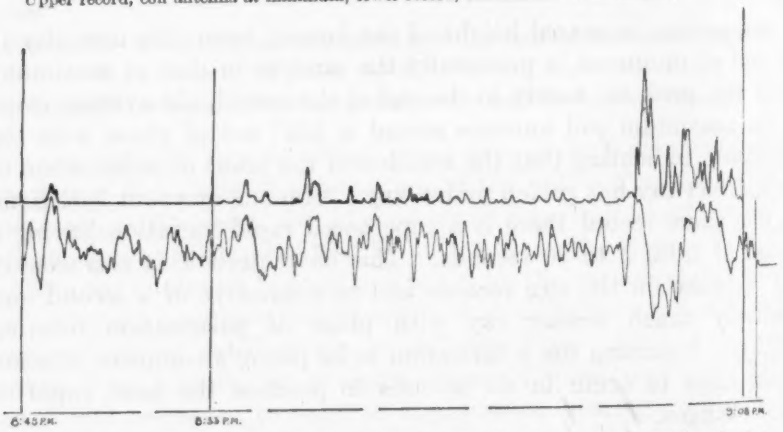

FIGURE 12.—*WMAL (1,240 kc), Washington, D. C., received at Kensington, Md., 13 km, June 6, 1928*

Upper record, coil antenna at minimum; lower record, coil antenna at maximum.

horizontal antennas are opposite in phase. It is interesting to note that the illustration given in that paper, however, shows clearly the

[6] T. L. Eckersley, Polarization and Fading of Short Wireless Waves, Nature, **121**, p. 707; May, 1928.

same sort of phase shifts between the two records as have appeared in the data of the present paper. To account for this phenomenon by an interference effect, at least two elliptically polarized indirect rays would be necessary, with their vertically polarized components undergoing changes in phase relationship similar to but lagging or leading those of the horizontally polarized components.

A more plausible explanation is that suggested for similar out-of-phase relations which occurred in the records made simultaneously on coil and vertical-wire antennas. If an indirect ray with rotating plane of polarization were arriving with an angle of incidence of nearly 90° and the plane of its arrival should gradually shift laterally from 0° to 45° with the maximum position of the coil antenna, the records made simultaneously by coil antennas in maximum and minimum positions would gradually shift from the 180° out-of-phase relationship to a nearly-in-phase relationship. If the angle of incidence were considerably less than 90°, similar changes in phase relationships would take place as the direction of arrival shifted to the 45° position, except that the two records would never come completely into phase. As the angle of incidence decreased still further, the two records would be more and more out of phase. If the indirect rays always arrive by means of a single reflection, the angle of incidence at the receiving end would increase with the distance between transmitting and receiving points, and a direction shift of given angle would produce a greater phase shift in the pair of fading records for a distant than in the pair for a nearer station because the incident ray for the former is more nearly horizontal. On the other hand, it should be possible for the ray from a nearer station to arrive at larger angles with the plane of the coil antenna in maximum position, since lateral radiation from the distant station would have to go to improbable distances to be reflected back at large angles. Very distant transmissions, furthermore, would presumably be received almost entirely in the great circle plane passing through transmitting and receiving stations. In the case of possible multiple reflections of the same ray or of an inverted U-shaped path the situation would be altogether different. Further measurements of the apparent effective height of the ionized region according to the method of Appleton and Ratcliffe, providing a sufficient variety of distances be covered, may give some useful information, for the method should prove most accurate and consistent for the distant stations if there are actual lateral reflections present.

As a partial check of the possible shifts in the direction of arrival of the indirect ray, observations were made simultaneously with three receiving systems utilizing, respectively, a coil antenna in maximum position, a second in the minimum position, and a third in a vertical plane at an angle of 45° with the other two. Comparisons

were made vocally by the three observers as changes occurred in the indicating galvanometers, since the third recorder for securing graphic records was lacking. Observing was done at a time when the phase relation between changes in the perpendicular coils was varying. The triple observations showed that for considerable periods the variations in the 45° coil were more nearly in phase with those in the coil at maximum, at times more nearly in phase with changes in the coil at minimum position, and for other periods considerably out of phase with both. Such effects do not prove direction shifts

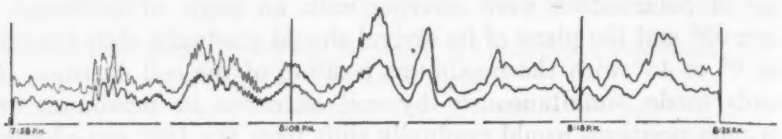

FIGURE 13.—*WJZ (660 kc), Boundbrook, N. J., received at Kensington, Md., 300 km, June 6, 1928*

Both records made on coils at maximum.

to exist but are similar to what would be expected if such shifts were real.

Figure 13 is typical of records taken from time to time to make sure that differences in simultaneous records were not due to the separation between receiving antennas. In all of these records made with similar antenna systems the simultaneous records showed that every variation, small and large, was in phase on the two records.

3. SIMULTANEOUS FADING RECORDS MADE WITH BARRAGE ANTENNA AND WITH VERTICAL SINGLE-WIRE OR COIL ANTENNA

Using the barrage combination of antennas to eliminate effects due to the ground wave, and the coil antenna in the maximum position

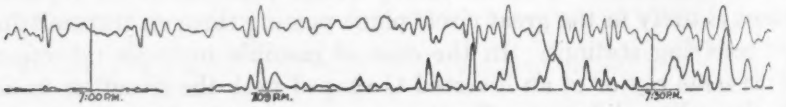

FIGURE 14.—*WBAL (1,050 kc), Baltimore, Md., received at Kensington, Md., 50 km, April 27, 1928*

Local sunset at 6.58. Upper record, coil antenna at maximum; lower record, barrage minimum.

to receive both ground and indirect rays, it was hoped that differences in records would indicate the amount of fading due to interference between these two rays. With the indirect ray remaining in the plane of the great circle connecting the two stations, changes other than those due to interference should have similar effects on the two receiving systems, though the magnitude of changes should differ.

Figures 14 and 15 show typical pairs of records. The earlier portion of the records of Figure 14 occurs during sunset before the angle of

incidence of the indirect ray has decreased sufficiently to produce more than a feeble horizontal component of the electric field. Consequently the intensity changes are quite feeble at first but increase as the ionized layer moves upward. During the first half of the records the intensity variations are in phase in the two antenna systems, indicating that these changes are produced farther back in the transmission path. The later portions of the records, however, show some

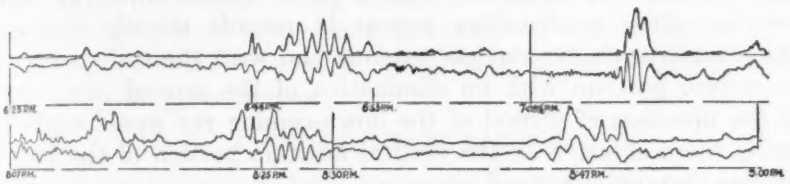

FIGURE 15.—*WBAL (1,050 kc), Baltimore, Md., received at Kensington, Md., 50 km, April 26, 1928*

Local sunset at 6.57. Upper record, barrage minimum; lower record, coil antenna at maximum.

changes in one antenna to be lagging similar changes in the other. Figure 15 shows similar lagging effects at approximately 6.44 to 6.53, 8.25 to 8.30, and 8.47 p. m. At other times this pair of records is usually in phase or 180° out. The latter condition is well explained by the fact that as the horizontal electrical component of the indirect ray increases, as shown by the barrage record, the vertical component presumably increases also and, being out of phase with the ground ray, whether partially or completely at these particular

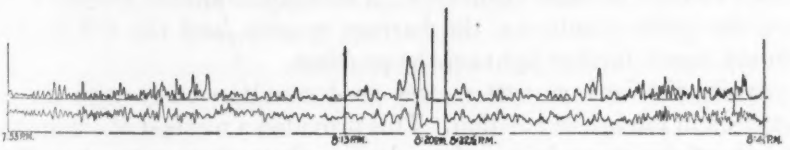

FIGURE 16.—*WBAL (1,050 kc), Baltimore, Md., received at Kensington, Md., 50 km, July 6, 1928*

Upper record, barrage minimum; lower record, vertical single-wire antenna.

times, causes a reduction of intensity in the coil antenna set at maximum position.

Figure 16 shows records made by a method similar to that last described except that a vertical single-wire antenna was substituted for the coil in maximum position. This method was used by Appleton and Ratcliffe.[7] Though the fading is more rapid in Figure 16, the phase relations between the records are similar to those of Figures 14 and 15, with less positive indications of the lagging effect because of the rapidity of variations. This effect does appear on a record [7]

[7] Reference 3, pp. 311-312, and fig. 9.

shown by Appleton and Ratcliffe, however. The explanation given by them that the difference in records is due to the interference between indirect and ground rays which can affect only one of the two receiving systems is a possible one for all of these pairs of records. Two facts, however, cast some question upon this as a complete solution: (1) It is doubtful if interference can account for the slight phase displacements in similar portions of the two records, as it may well account for the 180° out-of-phase relationships; (2) similar varying phase relationships appear in records already discussed, those made with the vertical antenna and with the coil antenna in maximum position with no elimination of the ground ray. Shifts in the direction of arrival of the down-coming ray would make the latter more effective on the vertical antenna portion of the barrage system than on either coil.

If rotating plane of polarization be combined with a direction shift in this ray, the phase relationships appearing in the pairs of simulta-

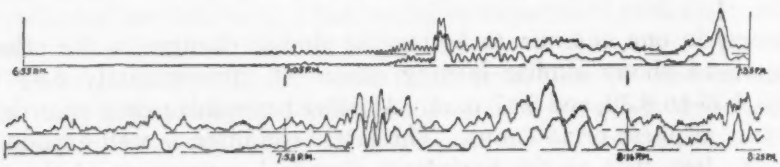

FIGURE 17.—*WBAL (1,050 kc), Baltimore, Md., received at Kensigton, Md., 50 km, March 30, 1928*

Local sunset at 6.30. Upper record, coil antenna at minimum; lower record, barrage minimum.

neous records become explicable. Three simultaneous records utilizing the vertical antenna, the barrage system, and the coil antenna should throw further light on the problem.

Again, the barrage system was used simultaneously with the coil antenna in minimum position. This provided a method of eliminating results of the ground wave from both coils so that remaining effects should be due to indirect rays only and to the angles which the coils made with that indirect reception. The effect of the entire vertical electric component of this ray should, of course, be eliminated in the barrage system. Figure 17 shows the type of record secured on transmission during the sunset period from a station only 53 km distant. The changes, both large and small, are very nearly of the same magnitude, and the larger variations are usually in phase on the two records. The phase relationships of the smaller periodic variations change considerably but are most often 180° out. In other words, this pair of records has much the same characteristics as appeared on the WJZ records, made with coils in maximum and minimum positions, in which the effect of the ground wave was practically absent because of great attenuation due to distance. There is in the early part of the records a superposed periodic varia-

tion suggestive of an indirect ray of small intensity with rotating plane of polarization and some shift in the lateral angle of arrival to cause changing phase relationships in the two fading records. The major variations would appear to be caused by a much stronger indirect ray of varying intensity with its plane of polarization unchanging at first but later rotating slowly, thus causing changes in one record to lag behind similar changes in the other. This rotation effect was not found in the records made by Appleton and Ratcliffe [8] with similar antennas. The intensity variations shown by their simultaneous records were so largely in phase that most of the fading could be explained by intensity variations occurring at some distance from the receiving antennas.

4. SHORT-PERIOD FADING

The rapid periodic fading previously mentioned and illustrated in Figures 9 and 17 should have some significance, since there is a considerable degree of regularity in its appearance, at least in reception from the two stations upon which observations have been most consistently made. During the cooperative investigation of fading conducted by the Bureau of Standards in 1925 this same phenomenon was noted,[9] though less consistently, in observations made at several different localities on transmissions from WGY (790 kc), Schenectady, N. Y. In the earlier case the phenomenon occurred for a few days at the spring equinox and was not found again. The newer cases were first noted at the same season but have continued for several months with very few exceptions whenever records were made. On the WJZ records this type of fading starts from 15 to 30 minutes after the Washington sunset and lasts in the vicinity of a half hour. On the WBAL records, which were made much less frequently, the start is likely to be practically at sunset, though there is some variation both ways.

The explanation of this phenomenon suggested in the earlier paper as an interference effect between ground and reflected rays is now proven unsatisfactory by the fact that this periodic fading is present even when the ground ray is absent. As previously stated, the fact that such fading is out of phase on records made with coils at maximum and minimum positions, respectively, makes any interference explanation difficult and suggests a relatively weak indirect ray with rapid rotation of its plane of polarization. No explanation is given at this time for the rotation itself.

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[8] Reference 3, p. 313, and fig. 10.

[9] Reference 2, pp. 437–439 and fig. 5, opposite p. 427.

IV. CONCLUSIONS

1. Considerable fading is caused by the fact that the indirect ray from a radio broadcasting station undergoes variations of intensity before arriving at the receiving antenna. This is proved by the fact that at times similar intensity changes occur simultaneously in coil antennas at maximum and minimum positions as well as in barrage antenna and coil at minimum.

2. Much evidence of fading caused by interference between ground and indirect rays is found in records of reception from transmitting stations sufficiently near to produce a ground wave at the receiving point. The nighttime intensity is often less than the daytime intensity which is due to the constant ground ray. The out-of-phase indirect ray often neutralizes the effect of the ground ray partially, and sometimes completely, even for short-transmission paths.

3. Direction shifts are apparently necessary to the explanation of phase displacements of less than 180° between otherwise similar records made simultaneously (1) with coil antenna at maximum and with vertical single-wire antenna, (2) with coil antenna at maximum and with barrage antenna, (3) with barrage and vertical single-wire antennas, (4) with coil antennas at maximum and minimum positions, and (5) with barrage and with coil antenna at minimum.

4. No proof of fading caused by fluctuating height of the ionized layer is found, but evidence of refraction of the indirect ray from a rising layer is found in the fact that the signal intensity in the coil antenna at minimum position starts at zero in daylight and gradually increases during sunset.

5. Rotation of plane of polarization of radiation refracted from the upper atmosphere is shown to be the cause of much fading, particularly, though by no means wholly, during the sunset period. The 180° out-of-phase relationship between records made simultaneously with coil antennas in maximum and minimum positions seems to demand this explanation. The cause of such rotation is not explained.

6. Reflections arriving by multiple paths are evidenced in records showing a periodic type of fading superposed on the main intensity variations and yet 180° out of phase on simultaneous records made with coil antennas in maximum and minimum positions. This fact makes the calculation of the effective height of the ionized layer by means of the sine of the angle of incidence, as determined by the method of Appleton and Ratcliffe,[10] somewhat doubtful, especially when measuring on other than distant stations.

7. The rapid periodic type of fading noted in a previous paper as occurring in signals from one station during the sunset period has been found to be quite common in the reception from two other stations.

[10] Reference 3, pp. 297-305.

The newer data point toward rotation of plane of polarization rather than interference as the cause.

As stated in the introduction, this investigation is far from complete. It is planned to make similar measurements over a much longer period of time to observe possible seasonal effects; to make simultaneous measurements by more than two receiving systems over a wider range of frequencies; to compare results of transmissions perpendicular to the earth's magnetic field with those parallel to it; to make direction and oscillographic observations simultaneously with the fading records; to make more quantitative measurements of these observations and compare calculated heights of the refracting layer, as determined by the angle of incidence method, on transmissions involving a wide range of distances, in order to note whether there is greater consistency in measurements on the more distant stations.

V. ACKNOWLEDGMENTS

Special acknowledgment is made of the assistance of H. S. Shaw, of Exeter, N. H., whose contribution of the salary of a research associate made possible the carrying on of this work at the Bureau of Standards.

Acknowledgment is also made of the assistance of S. A. Buckingham, R. P. Battle, and T. R. Gilliland in preparing apparatus and making the large number of records required in this work.

VI. APPENDIX

1. SUMMARY OF CONCLUSIONS OF PREVIOUS INVESTIGATIONS

Both Pickard, in his 1923 investigation,[11] and Appleton and Ratcliffe in their recent work [12] have given the chief credit for fading to intensity changes undergone in the path of the indirect ray. Pickard ascribes these changes to varying absorption and suggests a possible explanation, while Appleton and Ratcliffe find reason to suspect that interferences between rays traveling by multiple paths are the cause. These authors agree also in crediting interference between ground and indirect rays with a minor rôle in causing fading and practically eliminate direction shifts as a factor. Appleton and Barnett,[13] as well as Smith-Rose and Barfield,[14] had previously satisfied themselves that apparent direction shifts were due chiefly to elliptical polarization of the atmospheric ray and very little, if at all, to actual changes in lateral angle with the great circle plane through transmitting and receiving points. Pickard did not discuss changing angle of incidence nor rotation of the plane of polarization of the down-coming ray in

[11] Reference 1, pp. 152–158.

[12] Reference 3, pp. 314–315.

[13] E. V. Appleton and M. A. Barnett, On Some Direct Evidence for Downward Atmospheric Reflection of Electric Rays, Proc. Royal Soc. A, **109**, pp. 621–641; 1925. See especially pp. 623 and 635–636.

[14] R. L. Smith-Rose and R. H. Barfield, The Cause and Elimination of Night Errors in Radio-Direction Finding, J. Inst. of Elect. Engrs., **64**, pp. 831–837; 1926.

connection with his fading data. Appleton and Ratcliffe were unable to detect any evidence that these factors were affecting fading,[15] in spite of the fact that rotation of the plane of polarization of the incident ray had been accepted as explanation for apparent direction shifts. The Bureau of Standards report [16] on cooperative measurements in 1925, while accepting varying absorption as the more general cause of fading, gave considerable weight to interference effects so far as fading of nearer stations was concerned, but no data bearing upon the other factors were then secured.

While the present paper deals only with observations in the broadcast range of frequencies and with limited methods of analysis, it is well to have in mind the conclusions reached by investigations at other frequencies and by other methods. Working particularly with frequencies above 3,000 kc Breit and Tuve [17] found fading occurring independently of interference between ground and indirect rays and suggested multiple reflections and flickering effect due to wavy character of surface of the ionized region. Heising,[18] as well as Taylor and Young,[19] using an oscillographic method similar to that of Breit and Tuve found proof of a multiplicity of paths of different lengths. Heising found these regularly accompanied by fading and simultaneous with an apparent rising of the ionized layer. Rukop [20] in working with transmission of pictures at high frequency had earlier secured evidences of multiple paths which were accompanied by fading which, however, was not necessarily associated with the multiplicity of paths. The path length changed at times as rapidly as 50 km a second, giving the Doppler effect of a change in frequency at the receiving system. From theoretical considerations Pedersen [21] concluded that there should be an infinite number of downcoming rays at a given point on the earth's surface.

Fading produced by interference was found by Bown, Martin, and Potter[22] in an oscillographic study of the distortion in broadcast reception within a given area, and oscillographic observations by Friis[23] of reception on 18.75 megacycles proved consistent with the belief that fading is mainly caused by wave interference.

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[15] Reference 3, pp. 312–315.

[16] Reference 2, pp. 447–448.

[17] G. Breit and M. A. Tuve, A Test of the Existence of the Conducting Layer, Phys. Rev., **28**, pp. 554–575, September, 1926. See especially p. 564.

[18] R. A. Heising, Experiments and Observations Concerning the Ionized Regions of the Atmosphere, Proc. Inst. Radio Engrs. **16**, pp. 75–99; January, 1928.

[19] A. Hoyt Taylor and L. C. Young. Studies of High-Frequency Radio-Wave Propagation, Proc. Inst. Radio Engrs., **16**, pp. 561–578; May, 1928.

[20] Von H. Rukop, Die Bildtelegraphie als Untersuchungsmethode für die Ausbreitung der kurzen wellen, Elektrische Nachrichten-technik, **3**, pp. 316–318, 1926.

[21] P. O. Pedersen, The Propagation of Radio Waves Along the Surface of the Earth and in the Atmosphere, p. 230. Copenhagen, 1927.

[22] R. Bown, De L. K. Martin, and R. K. Potter, Some Studies in Radio Broadcast Transmission, Proc. Inst. Radio Engrs., **14**, pp. 57–131; February, 1926.

[23] H. T. Friis, Oscillographic Observations on the Direction of Propagation and Fading of Short Waves, Proc. Inst. Radio Engrs., **16**, pp. 658–665; May, 1928.

Very good evidence of real direction shifts was found by Friis[23] using a cathode-ray oscillograph to observe the phase difference of signal waves as received by antenna systems located a fraction of a wave length apart.

Changes in angle of incidence were found by Friis[23] to be much more frequent and of greater magnitude than direction shifts of the received signals. Heising, by his observations of signal retardation, had previously computed changes in angle of incidence sufficient to indicate rapid variations in the height of the ionized layer, sometimes as great as 72 km (45 miles) in two minutes.

Rotation of the plane of polarization of the indirect ray was suggested from theoretical considerations of the earth's magnetic field and varying ionization in the upper atmosphere by Appleton and Barnett[24] and by Nichols and Schelleng,[25] who indicated that this phenomenon might be expected in transmissions largely along the line of a magnetic meridian. Evidences of abnormal polarization causing apparent direction shifts were pointed out by Eckersley,[26] and Pickard[27] found by many observations made on high frequencies with an analyzer that the plane of polarization under certain conditions rotated 90° in transit. Alexanderson's investigation,[28] also on the high frequencies, seemed to indicate a continuous rotation of the plane of polarization with alternate points of plane and circular polarization along the transmission path. Hollingworth[29] recently made measurements to determine the state of polarization of the indirect ray which produces apparent progressive direction shifts during the sunset period, and on the basis of several assumptions calculated that the plane of polarization of an indirect ray received from a selected transmission of 21 kc rotated 90° during sunset and remained thus abnormally polarized during the night. Eckersley,[30] working with the high frequencies, made simultaneous fading records with horizontal and vertical antennas and reports that under some conditions the fading changes in the two records were so nearly opposite in phase as to indicate rotation of the plane of polarization of the indirect ray.

WASHINGTON, December 8, 1928.

[24] E. V. Appleton and M. A. F. Barnett, Wireless-wave propagation, Electrician, **94**, p. 398; Apr. 3, 1925.
[25] H. W. Nichols and J. C. Schelleng, The Propagation of Radio Waves Over the Earth, Nature, **115**, p. 334; Mar. 7, 1925; also Bell System Tech. J., **4**, pp. 215–234; April, 1925.
[26] T. L. Eckersley, The Effect of the Heaviside Layer on the Apparent Direction of Electromagnetic Waves, Radio Review, **2**, pp. 60–65, and 231–248; February and May, 1921.
[27] G. W. Pickard, The Polarization of Radio Waves, Proc. Inst. Radio Engrs., **14**, pp. 205–212; April, 1926.
[28] E. F. W. Alexanderson, Polarization of Radio Waves, J. Am. Inst. Elect. Engrs., **45**, pp. 636–640; July, 1926.
[29] J. Hollingworth, The Polarization of Radio Waves, Proc. Royal Soc., A, **119**, pp. 444–464; 1928.
[30] See footnote 6, p. 1066.

DETERMINATION OF THE SOURCE AND THE MEANS OF PREVENTION OF STONES IN GLASS

By Herbert Insley

ABSTRACT

The miscroscopic characteristics of different crystalline materials occurring as stones or lumps in glass are described and photomicrographs of stones originating from devitrification of the glass, incomplete solution of batch constituents, and incorporation in the glass of refractory wall material are reproduced. Methods of determining the location in the glass-making system of the source of stones, using microscopic as well as other methods, are given. Means of prevention or elimination of the stones are suggested.

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I. INTRODUCTION

In glass, "stones" are segregations of undissolved or crystallized material. The petrographic microscope has been found to be the only instrument which is generally useful in identifying the crystalline compounds in these stones. The optical constants, the general types, and the methods of identification of stones in glass have been reported in previous papers.[1] It is the purpose of this paper to show how the nature of the crystal assemblages, the shape and size of the crystals, and the amount of reaction between the stones and the molten glass indicate in what manner and from what material sources these stones originate and where in the glass-making operations they first appear. Possible methods for the prevention of different types of stones will also be discussed.

According to their source stones may be of three types—devitrification stones, batch stones, and refractory stones. Devitrification stones are the result of the crystallization of one or more of the constituents of the glass itself. Batch stones are due to the incomplete solution in the molten glass of one of the constituents of the batch. Refractory stones have their source in the walls of the pot or tank and they are introduced into the melt by spalling or by selective solution of the refractories.

[1] N. L. Bowen, J. Am. Cer. Soc., **1**, pp. 594-605; 1918. Herbert Insley, J. Am. Cer. Soc., **6**, pp. 706-716; 1923; **7**, pp. 14-18; 1924.

II. DEVITRIFICATION STONES

Crystallization in the glass, resulting in devitrification stones, is caused by improper batch compositions, improper temperatures in those stages of the manufacturing process where crystallization takes place, or by nonuniformities of composition within the melt. The local composition and temperature determine, of course, what compound, if any, will crystallize at any given point in the melt.

The accompanying photomicrographs of sections of devitrification stones (figs. 1, 2, 3, 4, and 5) show the different structures which are characteristic of the compounds crystallizing and of the conditions under which crystallization takes place. Figure 1 is a portion of a spherical group of minute tridymite (SiO_2) crystals. Many of these spherical aggregates—each from 1 to 2 cm in diameter—were formed in a random arrangement in a mass of glass which had lain for several days in the flow spout of a bottle glass tank at an estimated maximum temperature between 1,100° and 1,200° C. Evidently crystallization in this case can be ascribed to the long heat treatment to which the glass was subjected.

Figure 2 shows a thin section of wollastonite ($CaO.SiO_2$)"dog" taken from the bottom of a sheet-glass tank after the tank was shut down for repairs. The laminated appearance was produced by a series of fine threads which are composed of innumerable minute crystals of wollastonite. This structure indicates that crystallization was fairly rapid.

Figure 3 is a photomicrograph of a section of scum removed with a ladle from the melting surface of a sheet-glass tank. Dolomitic limestone was used in the batch, and, consequently, the crystals formed were diopside ($CaO.MgO.2SiO_2$) instead of wollastonite ($CaO.SiO_2$), the related compound which may crystallize when nonmagnesian limestone is used.

The compound $Na_2O.3CaO.6SiO_2$ has been found in several instances in plate and sheet glass. It may occur as large masses in the bottom of the tank or as individual crystals scattered through the finished sheet. Figure 4 shows a section taken from a mass of this material collected from the bottom of a tank. The radiating, feathery habit indicates either that crystallization was rapid or that the glass was unusually viscous.

In a glass used for making amber glass tubing with an automatic machine, a crystalline material was formed which appeared in the tubing as clots. A microscopic examination of this material showed it to be Jeffersonite (fig. 5), a compound related to diopside but which contains varying amounts of zinc and manganese. The glass itself contained oxides of iron, zinc, manganese, and magnesium as well as the customary soda, lime, and silica.

The detection of the place in the manufacturing process at which crystallization first occurs is of great importance in determining what

FIGURE 1.—*Hexagonal plates of tridymite (turned on edge) embedded in bottle glass*

Magnification × 50. Ordinary light.

FIGURE 2.—*Section of a mass of wollastonite crystals from the bottom of a tank*

Magnification × 35. Nicols crossed.

FIGURE 3.—*Diopside crystals in scum on the melting surface of a sheet glass tank where magnesian limestone was used in the batch*

The prismatic crystals show a tendency to radial arrangement about

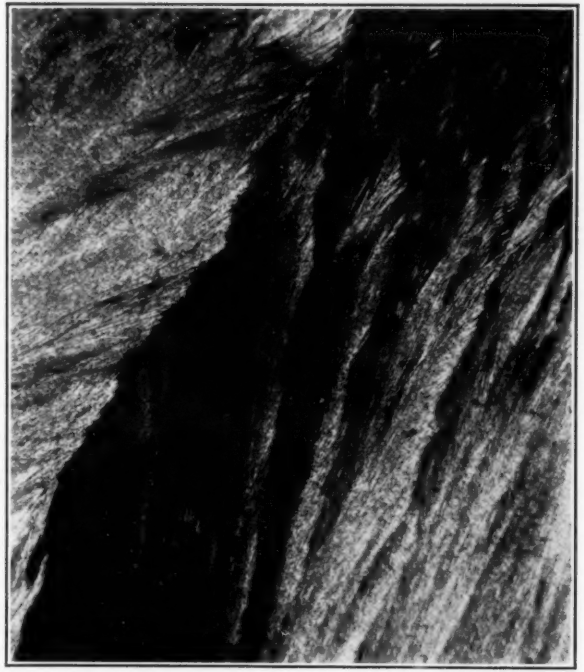

FIGURE 4.—*A mass of crystals of $Na_2O.3CaO.6SiO_2$ removed from the bottom of a sheet glass tank*

Magnification × 35. Nicols crossed.

steps should be taken to eliminate it. The microscope offers little aid in this connection. Usually the only method possible is to trace the devitrification from the point at which it is first seen back toward the melting operation, taking samples frequently and systematically.

When devitrification takes place along cords in the glass, it is probably caused by a higher concentration of one constituent in the cord than in the adjacent glass. In this case elimination of the cords may stop the devitrification. Nonuniformity of the batch or entrainment and remelting of scum are known causes of cordiness.

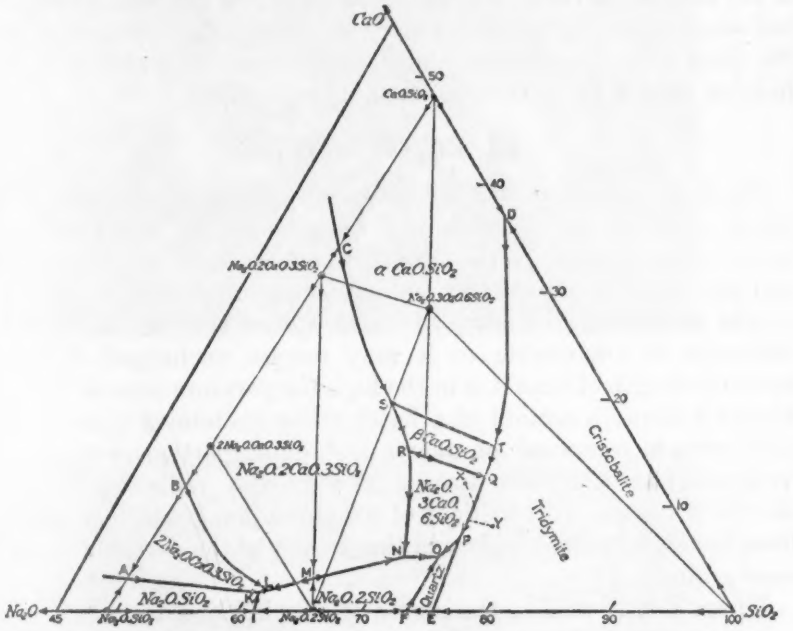

FIGURE 6.—*Crystallization diagram of the system $Na_2O.SiO_2$-$CaO.SiO_2$-SiO_2*

From Morey and Bowen, J. Soc. Glass Tech., **9**, pp. 226-264; 1928, on a weight per cent basis. Arrows indicate directions of falling temperatures.

Random distribution of devitrification stones throughout a glass melt indicates either that the composition of the glass is too high in the constituents crystallizing or that the glass is allowed to remain too long at temperatures favorable to crystallization. In the soda-lime-silica glasses containing only very small amounts of other oxides the nature of the compound crystallizing may be determined with the microscope and by reference to the equilibrium diagram of the system Na_2SiO_3-Ca_3SiO_2-SiO_2 (fig. 6),[2] the necessary direction of change of the glass composition can be determined. In general, the composition should be changed in the direction of falling temperatures indicated by arrows on the lines in Figure 6. For instance, the point

[1] Morey and Bowen, J. Soc. Glass Tech., **9**, pp. 226-262; 1925.

X (fig. 6) represents the composition of a window glass. If manufacturing conditions are such that this glass must be held at temperatures just below 1,000° for some time, devitrification may take place with separation of crystals of $Na_2O.3CaO.6SiO_2$. By changing the composition of the glass from *X* along the dotted line, the temperature at which crystallization takes place will be lowered and devitrification may be prevented. In the same way a bottle glass composition represented by the point *Y* may be changed along the dotted line to prevent crystallization of tridymite. When change in composition is not feasible, devitrification may frequently be prevented by raising the temperature slightly at the place where crystals occur and allowing the glass to cool rapidly through temperatures favorable to crystallization further on in the glass-making process.

III. BATCH STONES

Batch stones are caused by the incomplete solution of one of the batch constituents. Undissolved sand is by far the most usual source of such stones, although other sources, such as lumps of lime and segregations of coloring constituents, have been found. The quartz composing the cores of batch stones may be converted to tridymite or cristobalite or it may remain unchanged depending upon the length of time it is in the high temperature zone of the tank. Figure 7 shows a section of a batch stone containing circular areas with centers composed of quartz and outer portions composed of wedge-shaped tridymite twins. The needles radiating from the circular areas are cross-sections of tridymite plates which crystallized from the highly siliceous glass in the vicinity of the partially dissolved sand grains.

Where clay is used as the source of alumina in glass, batch stones sometimes result because of coarse grinding or balling of the clay. Their microscopic characteristics will be discussed with those of tank block stones which they resemble.

Four possible means of prevention of batch stones are:

1. Finer grinding of the batch.
2. More intimate mixing of the batch constituents.
3. Higher melting temperatures.
4. Longer melting time.

The scum so frequently found on the surface of the glass near the bridge in the melting chamber of bottle-glass tanks is caused by a combination of undissolved sand, devitrification products in the resulting highly siliceous surface of the melt, and drops falling from the silica brick crown of the tank. Figure 8 shows the upper portion of such a scum, collected from the surface of the glass in a tank after a shutdown. Note the roughly circular areas filled with small tridymite twins and surrounded by platy crystals of tridymite.

FIGURE 5.—*Jeffersonite crystals formed in glass tubing made with an automatic machine*

Magnification × 180. Ordinary light.

FIGURE 7.—*Section of a stone containing undissolved sand grains from the batch*

The quartz is largely transformed to tridymite, bright remnants of quartz grains remaining in two of the circular areas. The radiating needles are cross sections of tridymite plates resulting from an increased concentration of silica caused by a partial solution of the adjacent sand grains. Magnification × 70. Nicols crossed.

FIGURE 8.—*Section of the upper portion of the scum from the melting surface in a bottle glass tank*

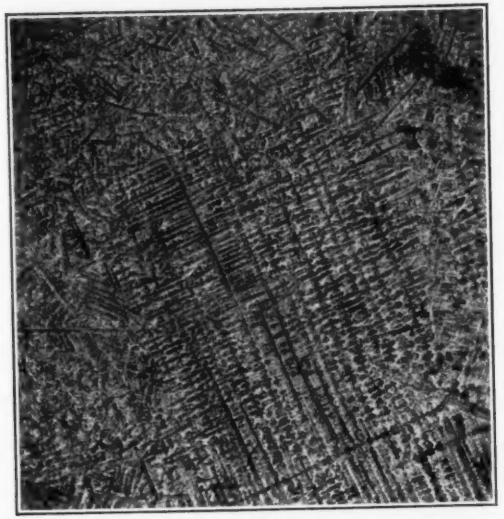

FIGURE 9.—*Section from the lower portion of scum from the melting surface in a bottle glass tank showing devitrification crystals of cristobalite*

Magnification = 50. Ordinary light

The formation of wedge-shaped tridymite twins is characteristic of the quartz to tridymite inversion, while the formation of plates is generally the result of crystallization from solution. The diameter of these roughly circular areas is only slightly less than that of sand grains usually used in the batch. A typical section of the lower portion of the scum is seen in Figure 9. Here the scum is composed almost entirely of cristobalite.

IV. REFRACTORY STONES

Refractory stones are derived from the walls of the containing vessels in which the glass is made. These vessels may be the melting tank, the flow spouts, or the pots or tanks from which glass is fed to the machines.

Two general types of stones derived from clay refractories can be recognized: (1) Those from above, and (2) those from below the glass surface.

Clay walls above the surface of the glass are attacked by the volatilized soda in the furnace atmosphere and by batch dusts composed largely of soda and lime. In the high temperatures of the melting chamber, corundum (Al_2O_3) and an alkali-aluminum-silicate liquid are the result of the reaction between the clay and the alkalies,[3] unless the clay block is extremely siliceous, and then the liquid silicate may be the only product of the reaction. Where faces of the clay block slope in the appropriate direction, the liquid silicate may flow into the molten glass carrying the crystals of corundum. Since corundum is not easily soluble in molten glass, these crystals frequently persist in the finished glass as stones.

The reaction between clay blocks and molten soda-lime glass where they are in contact is similar to that between clay blocks and the alkaline atmosphere of the furnace. Apparently in both cases the effect of the alkali, and probably of the lime, is to lower very markedly the temperature at which aluminum silicates dissociate into corundum and liquid and to permit this dissociation to take place in compositions fairly high in silica. In the system containing only Al_2O_3 and SiO_2 (fig. 10), mixtures with more than 55 per cent Al_2O_3 dissociate into corundum and liquid at 1,810° C. under equilibrium conditions. Microscopic examination has shown [4] that the dissociation into corundum and liquid takes place in burned clay in contact with soda-lime glass when the temperatures are those of commercial melting practice (below 1,550° C.) and when the clay block contains less Al_2O_3 than the molecular ratio $Al_2O_3.2SiO_2$.

A small amount of molten soda-lime glass penetrating into the clay walls or into the clay stones floating in the glass acts as a flux

[3] J. Am. Cer. Soc., **6**, p. 713; 1928. [4] J. Am. Cer. Soc., **7**, pp. 586-587; 1924; **9**, p. 638; 1926.

which induces an increase in the size of the mullite ($3Al_2O_3.2SiO_2$) crystals. At the same time the siliceous liquid remaining after the formation of mullite from the clay diffuses into the soda-lime glass. Continued action may lower the dissociation temperature sufficiently to cause solution of the mullite and simultaneous crystallization of corundum; except, infrequently, when the clay block contains so much silica that corundum can not be formed and solution of the mullite leaves only liquid. The liquid developed by the crystallization and later dissociation of mullite may partially crystallize as nephelite ($Na_2O.Al_2O_3.2SiO_2$). The fact that nephelite so frequently occurs as skeleton crystals surrounding mullite or corundum suggests

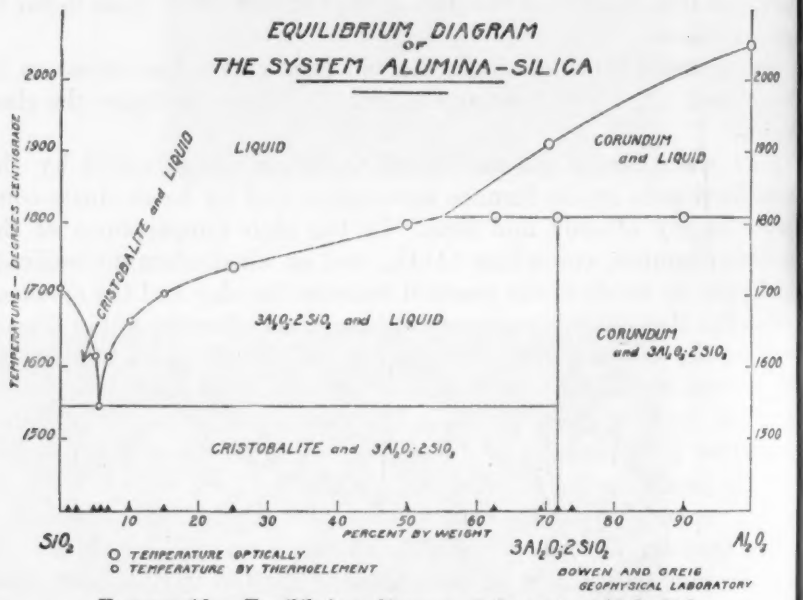

FIGURE 10.—*Equilibrium diagram of the system Al_2O_3-SiO_2*

From Bowen and Greig, J. Amer. Cer. Soc., 7, p 242; 1924.

that it forms during the cooling of the glass and not while it is at maximum temperatures.

The location of the source of refractory stones may be approximately determined from the size and nature of the crystals in them. Stones from blocks above the glass line usually are composed only of corundum. (Fig. 11.) Sometimes nephelite is present, and, rarely, large mullite crystals. The corundum crystals are always relatively large (more than 0.5 mm in width). A stone in which even the corundum has disappeared and only the reaction product (nephelite) remains is shown in Figure 12. Stones from tank blocks below the glass line in the hotter parts of the tank and clay stones from the batch are made up largely of corundum crystals with well-developed

FIGURE 11.—*A stone composed of large corundum crystals which had been carried into the glass from the surface of clay blocks above the glass line*

Magnification × 18. Ordinary light.

FIGURE 12.—*A stone composed entirely of nephelite crystals caused by long continued reaction between the molten glass and clay originally in the stone*

Magnification × 45. Nicols crossed.

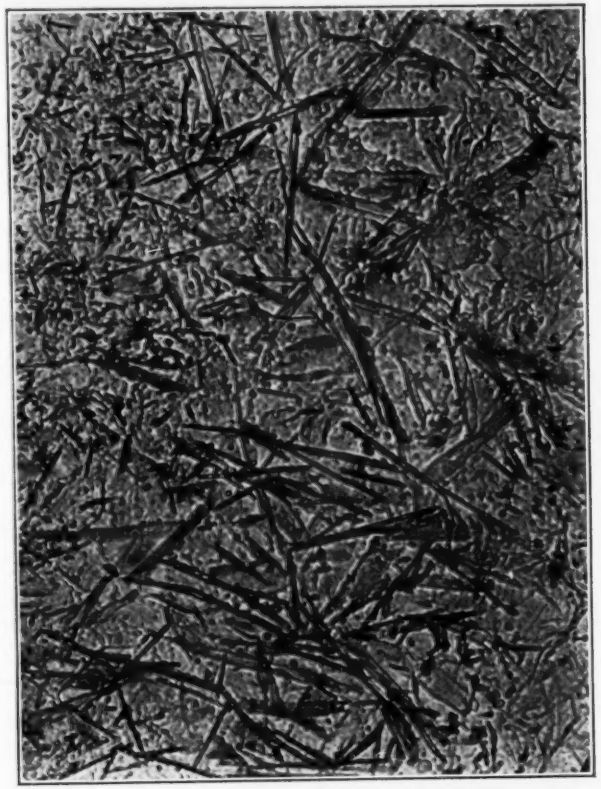

FIGURE 13.—*A stone derived from a clay block below the glass line in the melting end of a tank*

Reaction between the clay and the molten glass has been so extensive that the stone is composed very largely of minute plates of corun-

FIGURE 14.—*A clay stone which has undergone some reaction with the molten glass*

The quartz grains at the boundary of the stone are rounded and a few large mullite crystals have developed and separated from

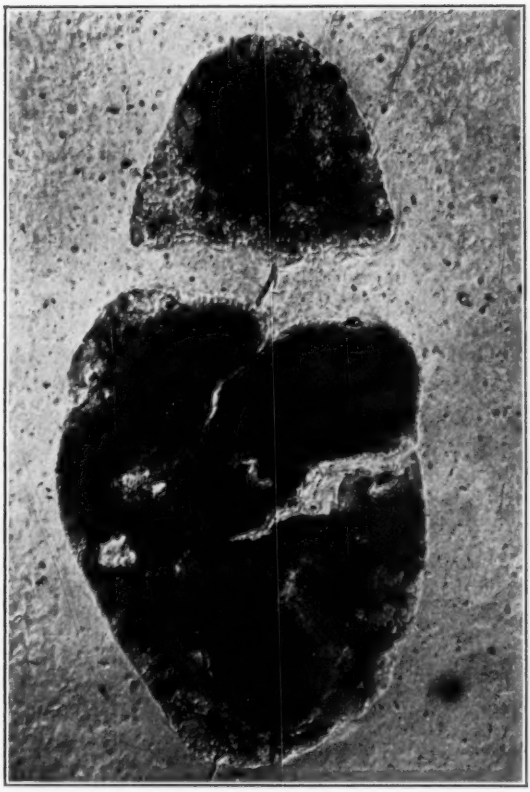

FIGURE 15.—*A clay stone which has undergone very little reaction with the molten glass*

Magnification × 160. Ordinary light.

mullite needles sometimes present. The corundum crystals from blocks below the glass line are always smaller than those from tank blocks above the glass line and are frequently very minute. (Fig. 13.) If the clay contained quartz grains originally, these are usually completely dissolved. In general, the crystals in such stones are not aggregated, but are somewhat dispersed. Nephelite is frequently associated with the corundum.

Stones from blocks in such cooler parts of the system as the refining end of the melting tank, the flow spouts, and the machine-feeding pots and tanks show much less reaction with the molten glass. A few minute corundum crystals may be found at the outer border of the stone, and quartz grains in the clay frequently remain undissolved. Mullite crystals may be large or small, but generally are in close-packed masses and show little tendency to be separated from the main mass of the stone except at the outer edge. Figure 14 shows a stone in which a small amount of reaction and solution has taken place. The quartz grains at the outer border of the stone are rounded and partially dissolved, and a few large mullite needles have developed and floated away in the glass. The stone shown in Figure 15 has been very little affected by the molten glass. Sharp corners have been rounded off, but no crystalline reaction products have been formed.

In melting operations using a batch containing clay there seems to be no microscopic method of distinguishing between clay stones from this source and stones given off by refractory blocks in the melting end of the tank. Both are very similar in microscopic appearance and in crystalline compounds formed. Once having determined with the microscope that the stones came from either of these two sources, a knowledge of the condition of the tank refractories and of the way the batch is mixed and ground must be relied on to make the distinction.

Microscopic examination of tank-block stones gives evidence of their point of origin in the glass-making system, but it gives no information as to how such stones may be eliminated. Usually either the offending blocks are replaced or they are backed with some sort of cooling arrangement.

Stones from blocks above the glass line are particularly annoying, since large crystals of corundum dissolve very slowly in molten glass. The greater the height to which clay walls extend above the glass line, the greater the danger from these highly insoluble stones. In designing tanks, consideration should be given to the advantages of eliminating clay blocks above the glass line on the side walls, the end of the melting chamber, and the bridge wall.

V. SUMMARY

The petrographic microscope affords a means of distinguishing between devitrification, batch, and refractory stones. Compounds crystallizing as devitrification stones are described and a method of determining the proper changes in temperature or composition of the melt to eliminate them is given. The characteristics of batch stones are enumerated and better grinding and mixing of the batch are suggested as means of prevention of this type of stone. The degree of reaction of refractory stones with the molten glass and the crystalline compounds formed are discussed; and they may be used as a means of determining the approximate location of the source of such stones.

WASHINGTON, January 2, 1929.

THE SPOTTING OF PLATED OR FINISHED METALS

By W. P. Barrows[1]

ABSTRACT

The American Electroplaters' Society, composed of foremen electroplaters, collected from their branches and from firms engaged in plating, funds to be used for researches on plating. The first problem selected for study was the "spotting out" of plated finishes, a defect which has proven very serious in such industries as the manufacture of builders' hardware.

The investigation showed that there are two quite distinct defects that have been commonly included under the term "spotting out." The "crystal spots" consist of dendritic crystals which appear only on metals having an "oxidized" surface; that is, one colored with copper sulphide or other sulphides and subsequently lacquered. The "stain spots" appear especially on cast metals, either plain or lacquered, in the form of discolored areas of irregular shape, usually with a small dark spot near the center.

The crystal spots have been found by X-ray examination to consist of cuprous sulphide (Cu_2S or chalcocite) growing usually between the layer of cuprous sulphide on the metal and the lacquer film. Their formation is caused or accelerated by sulphur in even minute amounts, such as may be derived from sulphur or hydrogen sulphide in the atmosphere or from rubber bands or wrapping paper or cardboard cartons. It was impossible to determine whether these traces of sulphur cause the slow formation of new cuprous sulphide in coarse crystals or the recrystallization of the very fine-grained cuprous sulphide already present.

The only promising remedies are (*a*) exclusion of sulphur from the surroundings, (*b*) the use of lacquers found to retard spotting, (*c*) the application of a thin film of a grease, such as petrolatum, to the lacquered surface, and (*d*) the use of wax paper for wrapping.

The stain spots are caused by the absorption in pores in the metal of acid or alkaline compounds during the plating process. Upon subsequent exposure to a high humidity such substances absorb moisture and exude upon and stain the surface. It was found that alkaline substances are especially difficult to remove from capillary pores. It is not practicable, however, to eliminate alkaline substances from the cleaning and plating solutions.

In some cases the porosity of the metal may be reduced by a change in pattern or in casting conditions. No method of rinsing or neutralizing was entirely effective in removing the compounds. Baking at high temperatures before lacquering is sometimes helpful.

The two most effective remedies are (*a*) permitting the chemicals to exude or spot out by exposing the articles to a high humidity before the final finishing, and (*b*) the application of a lacquer which has been found to retard this type of spotting. In general, phenol-condensation lacquers, which are less permeable to moisture than nitrocellulose lacquers, are also more effective in retarding stain spotting. Permeability to moisture is, however, not the only factor. Tests on many commercial lacquers of both types show that it is possible to develop lacquers which are much more effective for this purpose than the average nitrocellulose lacquers previously employed.

[1] Research associate of the American Electroplaters' Society.

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I. INTRODUCTION

During the past few years the American Electroplaters' Society has collected, through annual subscriptions from its branches and from firms engaged in electroplating, funds to be used for research on

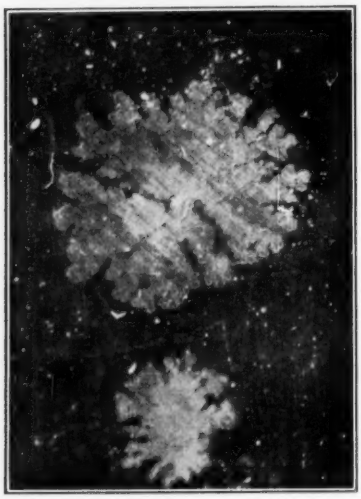

FIGURE 1.—*Typical appearance of crystal spots on sulphide finishes*

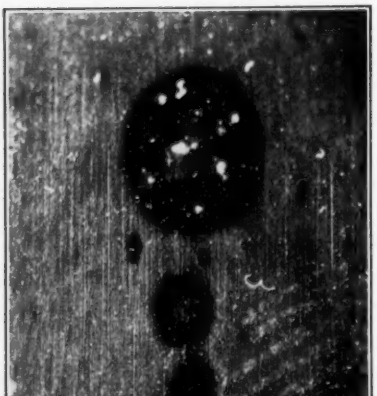

FIGURE 2.—*Typical appearance of stain spots caused by chemicals absorbed in pores*

electroplating. This "research fund" has been administered by the research committee of the society and has been used to pay the salaries and certain other expenses of the research associates stationed at the Bureau of Standards. At the suggestion of a number of manufacturers of builders' hardware who subscribed to this fund it was decided to study first a defect of plated metal finishes commonly referred to as "spotting out." This paper is a report of an investigation of that subject conducted by the author during the past two years.

While previous observations by platers had shown that there were different kinds of spotting out, the various types had not been clearly defined or described. Accordingly, a preliminary study of the subject was made through visits to plants and through the examination of specimens received from various sources. These observations showed conclusively that under the term spotting out, as generally used, at least two entirely distinct defects with unrelated causes are commonly referred to. In this paper these will be designated, respectively, as "crystal spotting" and "stain spotting," as these terms usually permit a ready identification of the nature and cause of the spots. These are illustrated in Figures 1 and 2.

Crystal spots occur only upon those metals which have on the surface a film of metal sulphide (commonly referred to as "oxidized" finishes) and a coating of lacquer or similar material. These spots are in the form of black or brown dendritic (treelike) crystals, often radiating from a center or nucleus, and varying in size from those just visible to the eye (or smaller) to those with a diameter of one-eighth inch (3 mm) or more. The formation of these spots is caused or accelerated by the action of sulphur or sulphur compounds.

Stain spots occur only on porous metals (usually cast metals) which have been subjected to the action of cleaning, pickling, or plating solutions, of which a portion has been retained in the pores, and on evaporation has left compounds in the pores. Upon subsequent exposure of the articles to air containing moisture, the latter is taken up by any deliquescent compounds present in the pores. The resultant solutions spread over the adjacent surface of the metal and form stains or spots of irregular area and variable color, either by their direct action on the metal or by the absorption of sulphur or other substances which discolor the metal.

It is usually possible to distinguish these two types of spots with the eye or with a lens of low magnification. If the sulphide finishes are applied to cast metals, it is quite possible for the two defects to occur upon the same article. In such cases the stain spots are likely to occur within a few days, while crystal spots may not appear until after some weeks or months.

In a discussion by A. K. Graham at the American Electroplaters' Society in Toronto, in June, 1928, it was pointed out that the above terms are not entirely exclusive, as the salts which exude from the pores may form crystals on the metal surface. Such crystals are usually light in color and are not likely to be mistaken for the characteristic dark crystals of metal sulphide. Confusion in terms may be avoided by referring, when necessary, to "crystal spotting of sulphide finishes" and to "stain spotting of porous metals."

On the same occasion reference was made to other terms proposed by G. B. Hogaboom to describe these two defects. The former was designated as "spotting in" and the latter as "spotting out." These terms refer to the fact that the sulphide crystals are formed by the action of sulphur from outside sources, while the stains result from compounds exuding from the pores. These terms may also be used, though here, again, the distinction is not sharp, as the "spotting out" (to form stain spots) requires the absorption of moisture from the surrounding atmosphere.

As the two types of spots are quite distinct in their composition and origin, they will be considered separately.

II. CRYSTAL SPOTTING

1. OCCURRENCE AND COMPOSITION OF CRYSTAL SPOTS

As will be noted later, there are a number of published references and discussions of spotting out, most of which obviously refer to the stain spots. Incidental recognition of crystal spots may be implied but is not clearly defined. At least there has been no known specific research published on this subject. Subsequent to the publication of progress reports of this investigation, N. E. Zadowski [2] described observations confirming the conclusion of the present author that sulphur causes the formation of crystal spots.

Information received from manufacturers indicated that the spotting of sulphide or oxidized finishes might occur either during storage in the plant or during shipment by train or boat. Practically all accounts agreed that the presence of sulphur in some form accelerated the formation of spots on sulphide finishes. While this type of spotting occurred at all seasons of the year, it was most noticeable from June to September.

Examination of spotted sulphide specimens received from the industry or produced in the laboratory showed that the spots occur only on lacquered finishes in the form of dendritic (treelike) crystals, usually with a black or nearly black color. The crystals grow initially between the lacquer film and the surface of the finish, although they may finally penetrate the lacquer film. Crystals

[2] Monthly Review, Am. Electroplaters' Soc., 15, No. 1, p. 4; February, 1928.

of this type growing between two planes pressed closely together are not uncommon in nature. Specimens were obtained [3] of magnetite (magnetic oxide of iron) entrapped between flakes of mica which exhibited the same dendritic crystal structure. Another example is the common moss agate.

The fact that these crystals can be formed when only copper and sulphur are present at least indicates that they consist of copper sulphide. Two forms of copper sulphide occur naturally—cupric sulphide (CuS) as the mineral covellite and cuprous sulphide (Cu_2S) as the mineral chalcocite. The crystals present in the spots are exceedingly thin and so light that it is impracticable to collect enough for a chemical analysis. Mineralogic and petrographic examination also failed to identify the crystals. It was therefore decided to make an X-ray examination.[4] A small amount of the crystals was obtained by removing the lacquer with butyl acetate, after which the crystals could be floated or brushed off the surface without disturbing the underlayer of black copper sulphide. Some of the latter was also scraped off for comparison. The crystals from half a dozen specimens filled a capillary tube 10 by 0.5 mm. The method consisted in comparing the X-ray diffraction pattern of the crystals directly with that of other substances of known composition. Comparisons were made by placing the materials in the opposite ends of the same capillary tube, separating the two substances with a cotton plug, and projecting the two patterns on the same film.

In this way comparisons were made between (*a*) the black sulphide present in the sulphide coating, (*b*) the crystals removed from the surface, (*c*) the mineral [5] chalcocite, (*d*) the mineral covellite, and (*e*) cupric oxide. The results showed conslusively that the patterns of (*a*), (*b*), and (*c*) were identical and quite different from those of (*d*) and (*e*). It is evident, therefore, that both the original coating and the crystals which formed on it, consist of cuprous sulphide, Cu_2S.

The crystals of cuprous sulphide may conceivably be formed in either of two ways; (*a*) by a recrystallization of the much finer (but also crystalline) coating of cuprous sulphide produced by the action of polysulphides on the copper or (*b*) the formation of new cuprous sulphide by the slow action of sulphur upon minute areas of copper that may be exposed through the original sulphide film. The latter view is rendered more probable by the fact that (1) the crystal formation is accelerated by sulphur vapor and (2) the crystals are more likely to form where there is a slight scratch which may penetrate not only the lacquer but also the sulphide film. At best, it is difficult to fully explain the formation of these crystals. It is possible that

[3] Through the courtesy of E. T. Wherry, of the United States Bureau of Chemistry and Soils.

[4] All X-ray analyses were made by F. Sillers, jr., of the Bureau of Standards.

[5] The author is indebted to H. E. Merwin, of the Geophysical Laboratory, for these mineral specimens.

the presence of small amounts of sulphur simply accelerates the formation of the visible crystals by the recrystallization of the finer-grained coating of cuprous sulphide.

2. FACTORS INVOLVED

(a) METHOD OF TEST EMPLOYED

Because the occurrence of crystal spots is not uniform or quantitative under most conditions, it was necessary to subject at least 10 or 20 specimens to each set of conditions to obtain reliable "average" performances. Most of the specimens were prepared in the laboratory, but whenever feasible corresponding plant samples were included in the tests. All specimens were dip lacquered unless otherwise stated.

In order to obtain at least comparative results in a short time, an accelerated test was developed after certain preliminary experiments had been made. Unless otherwise stated, the tests were made by storing the specimens in contact with rubber bands or flowers of sulphur. Under these conditions spots usually appeared within one to three days, while in many cases in the absence of sulphur or rubber one to three months elapsed before the appearance of the spots.

(b) THE BASE METAL

In order to determine whether the metal on which the sulphide finish is applied affects the tendency for the crystal spots to form, tests were made with sulphide finishes on sheet copper and brass and on sheet steel plated with copper or brass. The results showed that there is no difference in the behavior of these metals. It is evident, therefore, that the crystal spots are connected with the copper itself and not with the metal underlying it.

(c) THE SULPHIDE FILM

(1) Composition of the Film.—Experiments were made with black films produced on copper or brass by (1) the action of sodium or potassium polysulphide solutions, (2) black nickel plating from sulphocyanate solutions, (3) black nickel plating from nickel chloride solutions containing no sulphur, (4) copper carbonate black, and (5) films produced on silver-plated steel by polysulphide solutions. The results showed that spots appeared only on (1), (2), and (5); that is, those in which sulphur was present. It is interesting to note, however, that while crystal spots can be produced by sulphur acting upon black nickel deposits from sulphocyanate solutions and upon silver sulphide finishes, there is little evidence that crystal spots occur on commercial products of these types.

Although crystal spots appeared on copper sulphide finishes in large numbers within a week, they did not appear on silver sulphide

until after 8 to 12 weeks' exposure in contact with sulphur, and on black nickel they remained small and inconspicuous after 6 weeks' exposure to sulphur, although they appeared after a week's exposure. Tarnish was more readily produced on the bright areas of relieved silver sulphide films than were crystal spots. While the spots produced on silver sulphide resembled somewhat those formed on copper sulphide, they were more leaflike in appearance. A crystallographic examination [6] of the spots appearing on silver sulphide finishes indicated that they consist of silver sulphide, Ag_2S, having the crystal form of the mineral acanthite.

(2) PREPARATION OF THE FILM.—In order to determine whether any of the materials other than the sulphide used in the preparation of the sulphide films were responsible for the spots, films were produced by exposing to hydrogen sulphide copper that had not been in contact with any acids or alkalies. The black film so produced resembled that made with sodium or potassium polysulphide and showed the same tendency to form crystal spots. As nothing but copper sulphide and water can be formed in this reaction, it is evident that neither acids or alkalies are necessary for the formation of these spots.

(d) THE PROTECTIVE COATING

(1) RELATION OF LACQUER TO SPOTS.—Experiments with lacquered and unlacquered specimens showed that although certain conditions, such as exposure to sulphur, would cause discoloration of the unlacquered specimens, no crystal spots appeared except on the lacquered specimens. Evidently the presence of a film of lacquer or of some similar material is necessary for the formation of such crystals.

(2) COMPOSITION OF THE LACQUER.—As the crystals apparently grow between the surface of the sulphide film and the lacquer film (at least initially, although they may penetrate the lacquer film later), it appeared possible that by increasing the adherence of the lacquer the formation of the spots might be retarded or prevented. Over 20 experimental nitrocellulose lacquers were prepared and tried out for this purpose. Although none of these lacquers entirely prevented spotting out, those containing linseed oil showed a marked improvement in this respect. The improvement was most marked in those lacquers containing the highest proportions of linseed oil. Unfortunately, however, lacquers containing linseed oil show a tendency to discolor the finish on both the dark and relieved portions, and hence their use is impracticable.

Preliminary experiments indicated considerable differences in the rate of crystal formation on sulphide finishes lacquered with different types of lacquers. Later in this paper detailed reference is made to

[6] By H. E. Merwin, of the Geophysical Laboratory of the Carnegie Institution.

more extensive tests on a large number of commercial and experimental lacquers.

(3) THICKNESS OF THE LACQUER FILM.—Experiments indicated that the thick layers of lacquer produced either by applying two or more coats, or by using less thinner, retard the formation of crystal spots. The rate of formation was retarded by thicker coats of all lacquers tested. For a given type of lacquer the retardation was approximately proportional to the thickness of the film.

(4) SUBSTITUTES FOR LACQUER.—In order to determine whether transparent coatings other than lacquers are beneficial, experiments were made under accelerated conditions with shellac and linseed-oil varnish. With the shellac coating, crystal spots were produced as readily as with lacquer. With spar varnish there was little or no formation of crystal spots, but the varnish reacted with the copper sulphide and acquired a green color. It was therefore unsatisfactory.

(5) SULPHIDE PARTICLES IN THE LACQUER.—It was suggested that the presence of suspended particles of copper sulphide scraped or washed off of the "oxidized" surfaces during the lacquering might accelerate the spotting. Some of this sulphide was therefore scraped off and mixed with lacquer which was then applied. Portions of the sulphide were also applied to the surface of other specimens whose lacquered film contained no sulphide. After several months' exposure in the absence of any other accelerating agent there was no evidence that the presence of such particles either in the lacquer or in contact with the surface affected the formation of crystals.

(6) ACIDITY OF THE LACQUER.—Following a suggestion that free acid in the lacquer might cause or accelerate the spotting, experiments were made with carefully neutralized lacquers and with lacquers containing appreciable free acid. Lacquers containing free acid tarnish the surface but do not affect the crystal spotting.

(7) COMPARISON OF LACQUERS.—Preliminary experiments on the rate of formation of crystal spots under different types of lacquer films led to a more extensive investigation in order that the published results should be representative of the commercially available materials. Manufacturers were invited to submit samples either of their usual make or of experimental lacquers, which were believed to be superior in resistance to penetration by sulphur or moisture. These lacquers were tested with respect to both crystal spotting and to stain spotting. The results of the latter tests are tabulated under Section III of this paper.

The results of the lacquer tests are tabulated without reference to the source of the lacquers, but the firms have been furnished the key numbers of their own samples as a guide to possible improvements. Since it was impracticable to determine the exact composition or reproducibility of any lacquer sample, and it was undesirable to

report the results by trade or firm name, samples are identified by number, and so far as possible by type, as designated by the makers.

All lacquers were applied by dipping, as this probably represents the simplest and most reproducible procedure, and were tested in the following manner:

Test for crystal spotting of copper sulphide finishes.—As the results obtained with sheet copper were the same as those with a copper-plated surface, the former was used in the tests. Strips of rolled sheet copper—for example, 2.5 by 10 cm (1 by 4 inches)—were given the following treatment. At least 10 specimens were used in each set.

Scrub the surface with powdered pumice and water and rinse in cold water.

Immerse the piece in a warm (105° F.) solution of potassium polysulphide, prepared by dissolving 3 g of potassium hydroxide in 100 ml of water, adding 3 g of flowers of sulphur and boiling for 15 minutes or until the solution assumes a dark-brown color. The solution is then filtered and diluted to 1 liter. The immersion is continued until the surface assumes a uniform black color, usually in one minute.

Scratch brush the surface lightly with a brass wheel and water and rinse and dry.

Dip in lacquer, allow to drain, and apply whatever subsequent treatment, such as baking, is suitable for the lacquer employed. In order to produce lacquer films of approximately the same thickness the lacquer is first diluted with the thinner until it just produces an iridescent film on a dipped metal specimen. Sufficient lacquer is then added to just prevent the formation of iridescence.

Wrap each specimen in high-grade white filter paper, and sprinkle fine flowers of sulphur over the surface of the paper. Store the specimens in a closed vessel; for example, a desiccator, at room temperature 20° to 30° C. (68° to 86° F.), and examine at intervals; for example, every 24 hours, for two weeks. Record the number, size, and time of appearance of the crystal spots.

The production of lacquer films of approximately equal weight per unit area by the above method was tested by weighing the dried lacquer films. Very nearly the same weight was obtained with all lacquers except No. 4, 12, and 22, films of which weighed approximately one-half as much as the others. This does not mean that these lacquer films were necessarily thinner than the others (with the exception of No. 22, which produced a somewhat iridescent film from the unthinned lacquer as received). Possibly the dried films of some lacquers have lower specific gravities than do the films from other lacquers. No attempt was made to determine these specific gravities.

Twenty specimens consisting of two lots of 10 specimens each were employed in each lacquer test. To minimize the effects of accidental

conditions which might change from time to time, the two lots of specimens for testing each lacquer were prepared on different days. The results in Table 1 are the average values for both lots. The average values of one lot in the same test did not vary in any case by more than 20 per cent from the average value of the companion lot.

TABLE 1.—*Tests of commercial and experimental lacquers for crystal spotting*

[In contact with sulphur]

Lot No.	Type of lacquer as designated by the maker	Temperature of baking		Time required to produce crystal spots	Time required to produce crystal spots that cause rejection
		° C.	° F.		
	GROUP I				
				Hours	*Hours*
2	Not designated	50	122	84	156
6	do	50	122	72	180
9	do	50	122	84	156
11	do	50	122	36	156
16	Synthetic resin	50	122	96	180
[1] 16a	do	50	122	156	424
17	Not designated	50	122	84	180
19	do	50	122	96	168
	GROUP II				
3	Nitrocellulose	50	122	24	72
4	Not designated	50	122	24	60
5	do	50	122	24	48
7	Nitrocellulose and natural resin	50	122	24	60
8	Not designated	50	122	24	48
10	Nitrocellulose and gum	50	122	24	48
12	Not designated	50	122	24	60
[1] 12a	do	50	122	48	96
13	Natural gum and nitrocellulose	50	122	24	84
14	Synthetic gum	50	122	24	60
18	Not designated	50	122	36	72
20	do	50	122	24	60
21	do	50	122	24	72
23	do	50	122	36	72
	GROUP III				
1	Phenol-condensation resin	135	275	12	24
15	do	135	275	12	24
22	Not designated	50	122	12	24
24	do	135	275	12	24

[1] Specimens 12a and 16a had thicker lacquer coatings than the others.

The lacquers tested have been divided roughly into three groups. The samples coated with lacquers in Group I were least affected by contact with sulphur. Visible spots did not form until after 72 hours exposure (with the exception of No. 11). The crystal spots did not grow to objectionable size until after 156 hours.

The samples coated with lacquers of Group II are considerably more affected by sulphur than those of Group I. Visible crystal

spots appear with these lacquers in approximately 24 hours. The spots do not grow as fast as those on specimens coated with Group III lacquers and do not reach the point of rejection until after at least 48 hours.

The samples coated with lacquers in Group III are extremely susceptible to the effects of sulphur as exhibited by the rapid formation of crystal spots. Crystal spots appear visible to the eye on surfaces coated with these lacquers in approximately 12 hours after exposure. Within 24 hours, the spots have grown sufficiently in size and number to cause rejection of the specimen.

The ratio of the time for the first appearance of the crystal spots to that necessary for sufficient growth to cause rejection of the specimens was (with the exception of lacquer No. 11), between 1 to 2 and 1 to 3, thus showing a general parallelism between the two stages of failure.

Two types of crystal growth were noted. With lacquers of Groups II and III, with one or two exceptions, the crystal spots grew beneath the lacquer film and could not be removed by rubbing the surface. The crystal spots with lacquers of Group I, however, while they initially grew beneath the lacquer, tended to penetrate the film after a short period of growth. At the end of the run the crystal spots had penetrated the lacquer to such an extent that they could be almost entirely removed by rubbing the surface. In general, the crystal spots were much smaller on specimens coated with Group I lacquers than those coated with Group II and III lacquers.

In order to amplify the preliminary experiments on the effect of increasing the thickness of the lacquer film on the rate of crystal growth, the films of lacquer No. 12 (Group II) and No. 16 (Group I) were increased to about 250 per cent of their previous thickness by applying a single coat of a less diluted lacquer. It will be noted from the results of these tests (12a and 16a in Table 1) that an increase in the thickness of the lacquer film produced an approximately proportional increase in the time required for the appearance and growth of the crystals.

In connection with the above tests, strips of bright copper were coated with the same lacquers and were kept in contact with sulphur for from four to six weeks. During this period practically no tarnish appeared on any of the specimens, although unlacquered copper strips turned dark in a few days under these conditions. Evidently none of these lacquers permit much sulphur to pass through. These results show that there is no necessary relation between the permeability of a lacquer to sulphur and its ability to retard the formation of the crystal spots.

(8) Effect of a Film Superimposed on the Lacquer.—Experiments proved that a grease film, applied to the lacquered surface by

dipping the articles in a dilute solution—for example, 4 per cent or less of petrolatum in carbon tetrachloride—retards the formation of crystal spots in the presence of sulphur. Crystal spots formed on ungreased specimens in contact with sulphur within 1 to 4 days, whereas spots did not appear on specimens with the petrolatum film until after 10 to 13 days. Since the preliminary announcement of the above procedure it has been reported that in one plant a paraffin oil has been successfully employed as a protective film on lacquered oxidized finishes.

(e) THE ENVIRONMENT

(1) SULPHUR.—Contact with sulphur is the most rapid means of accelerating the formation of crystal spots. If the surfaces are sprinkled with flowers of sulphur, spotting usually occurs within 1 to 4 days. Even in this case, however, it is probably the sulphur vapor produced by the very slow evaporation of the sulphur that causes the spots. Experiments with lump sulphur contained in the same vessel with the specimens but not in contact with them showed that it also accelerates spotting, but not nearly so rapidly as does the fine sulphur. (Lump sulphur may require as much as 40 to 50 days to cause spotting.) It is also possible that the sulphur dissolves in the lacquer film and thus passes through it.

(2) RUBBER.—Rubber usually contains free sulphur, and in these tests it was found to produce the spots as readily as does powdered sulphur. That the effect of ordinary rubber is due principally to the presence of free sulphur on the surface and its evaporation is evident from some experiments with a special "nonblooming" rubber that contains little or no free sulphur. It was found that with the nonblooming rubber only about one-third as much spotting is produced as with ordinary rubber.

(3) SULPHUR COMPOUNDS.—Experiments with air containing from 0.1 to 1.0 per cent by volume of hydrogen sulphide showed that with even the lowest concentration crystal spots occur, but not so rapidly as with free sulphur. The hydrogen sulphide also causes tarnish. Air containing 1 per cent of sulphur dioxide causes rapid tarnish of the specimens but no formation of crystal spots.

(4) WRAPPING MATERIALS.—Extensive experiments have shown that the spotting may be accelerated by contact with certain papers, such as kraft papers or cardboard boxes, employed in wrapping or storing the specimens. Actual contact with the paper appears necessary to produce the spotting. Thus, when groups of two or more specimens, so wrapped that the paper came in contact with only one side of each plate, were stored in a closed desiccator containing only these specimens crystal spots appeared solely on the side of the plate in contact with the paper. It is difficult, however, to show a

direct relation between the sulphur content of the paper and the effect on spotting. Filter paper with only 0.0007 per cent of sulphur caused about as much spotting as kraft paper with 0.002 to 0.003 per cent or cellophane with 0.005 per cent of sulphur. It is equally difficult to attribute the spotting to any constituent of the paper other than the sulphur. In addition, paper does not produce spotting quantitatively. Thus, while all specimens of the same lot of sulphide finishes in contact with sulphur will spot at very nearly the same rate, only part of the specimens will spot at all when wrapped in paper. It is quite possible that the sulphur present in paper may be localized and, hence, produce spotting only on specimens or portions of them that are adjacent to high concentrations of sulphur in the paper.

Determination of sulphur in paper.—The various methods that have been used or suggested for detecting or determining sulphur in paper all relate to the sulphur which is present as sulphide or in some form that may evolve hydrogen sulphide under certain conditions. Inert substances, such as calcium sulphate, that may be used as fillers are not included in the determination of sulphur as conducted for this purpose. Among the methods suggested are (*a*) wrapping polished silver in the moistened paper and determining the extent of the tarnish; (*b*) heating the paper with zinc and hydrochloric acid, bringing the evolved hydrogen sulphide in contact with moist lead acetate paper, and noting the color produced; and (*c*) treating the paper with zinc and hydrochloric acid, passing the gases into an alkaline cadmium solution, and titrating the hydrogen sulphide by the method used in determining "evolution sulphur" in steel. Of these (*b*) was found most promising for our purposes. Method (*a*), while undoubtedly a valuable practical method for detecting some minimum amount of sulphur, does not give quantitative values. Method (*c*) is difficult to apply with small samples of paper, and with large samples it is difficult to expel all the sulphur. The following method is based upon the "official paper testing methods of the pulp and paper industry," and upon modifications suggested in a personal communication from B. Egeberg, of the International Silver Co.

Apparatus.—The special apparatus required for this determination consists of a 500 ml round-bottom flask having the connections and dimensions shown in Figure 3. All gases generated in the flask pass through a filter paper which is clamped between the mouth of the flask and the end of the tube.

Specimen.—The specimen consists of 0.25 to 1.0 g of paper (depending on the sulphur content) either ground or thoroughly disintegrated by shaking with distilled water.

Reagents.—Small pieces of C. P. stick zinc free from sulphur and arsenic are activated by adding 10 ml of a solution containing 1 g/l of $CuSO_4.5H_2O$ (or 0.25 g/l of copper) to each gram of zinc. After allow-

ing the solution to stand a few minutes for the deposition of the copper, wash the zinc with distilled water until free from zinc sulphate. The zinc can be reactivated several times.

Concentrated C. P. hydrochloric acid free from sulphur and arsenic.

C. P. lead acetate, 100 g/l of $Pb(C_2H_3O_2)_2.3H_2O$.

C. P. sodium thiosulphate solution, containing 3.9 mg/l of $Na_2S_2O_3.5H_2O$. Each milliliter of this solution contains 0.001 mg of sulphur, all of which is evolved as hydrogen sulphide. This is equivalent to 0.0001 per cent of sulphur in a 1 g sample.

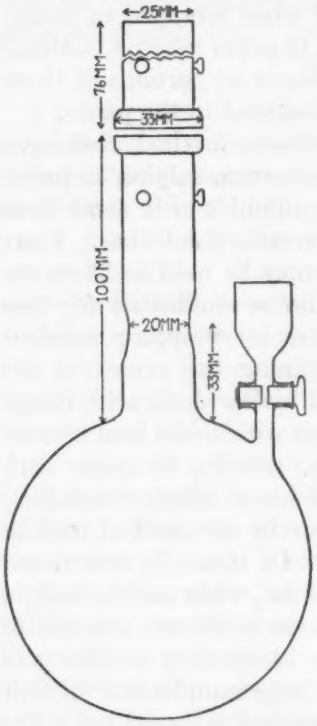

FIGURE 3.—*Apparatus for the determination of sulphur in paper*

Sulphur-free cotton, prepared by boiling surgical absorbent cotton in a dilute solution of sodium hydroxide and washing thoroughly with distilled water.

Transfer the weighed specimen to the flask with 80 ml of distilled water and add approximately 2 g of activated zinc. Insert in the neck of the flask at the constriction a loose wad of surgical absorbent cotton. Clamp between the mouth of the flask and the tube a hardened filter paper (such as Schleicher and Schüll's 575) which has been freshly moistened with a 10 per cent solution of lead acetate. Rubber bands may be employed for clamping the filter paper into place between the tube and neck of the flask without danger of contamination if sufficient care is taken. Place another wad of absorbent cotton in the tube above the filter paper. Prepare flasks under duplicate conditions containing in place of the paper under test pure sulphur-free cotton and measured amounts of sodium thiosulphate solution. Add to each flask 20 ml of concentrated hydrochloric acid and set all the flasks on the steam bath. At intervals of 15 minutes remove them to a hot plate and heat the solution to the boiling point until moisture just begins to condense in the neck of the flask beneath the cotton plug. Return to the steam bath, and after 15 minutes repeat the boiling on the hot plate. After three such treatments, requiring a total of about 50 minutes, replace the lead acetate paper with a fresh piece and repeat the heating and boiling. If, as is usually the case, no stain is produced on the second paper, the color of the first paper serves to measure the sulphur content of the sample. If the second paper is darkened,

it is better to start a fresh determination, using a smaller sample, in order that all the sulphur may be evolved in a convenient period. The percentage of sulphur present is found by comparing the depth of the color developed by the sulphur from the specimen with that developed from known amounts of sulphur evolved from the thiosulphate solutions. Blanks on the reagents should accompany every determination.

As 0.000001 g of sulphur will give a distinct stain, care must be taken to protect the paper under test from contamination. It must be protected from atmospheric fumes and should not be handled with bare hands. The evolution of hydrogen is insufficient to completely remove the hydrogen sulphide from the flask; hence it is necessary to heat the contents of the flask to the boiling point for short periods. More concordant results were obtained by this procedure than by simply warming the flask. Very pure zinc at times reacts rather slowly with dilute hydrochloric acid even after activating with copper. It is possible to hasten the reaction by employing platinum wire in contact with the zinc as an additional activating agent.

The following table contains the average results, obtained in several determinations by the above method, of the active sulphur content of samples of typical materials which have been or might be employed for wrapping hardware:

TABLE 2.—*Active sulphur content of wrapping materials*

Materials	Active sulphur
	Per cent
1. Kraft paper A	0.0025
2. Kraft paper B	.0020
3. Kraft paper C	.0030
4. Washed filter paper	.0007
5. Cellophane	.0050
6. Heavy white waxed paper	.0012
7. Semiwaxed kraft paper	.0027
8. Full waxed kraft paper	.0020

Experiments were made upon the use of wax paper and tin foil as substitutes for kraft paper. The use of waxed papers is not original but was suggested by the experience of several plants.[7] The effect of petrolatum films was also included in these tests.

Seventy specimens of sulphide finishes were exposed wrapped in waxed paper and divided into two portions—one lot in an atmosphere approaching 90 per cent humidity in closed desiccators and the other lot under uncontrolled humidity conditions but stored where there was no danger of contamination from sulphur. At the same time

[7] Communicated by R. E. Hicks, E. G. Anderson, and others.

approximately the same number of specimens were stored under the same conditions wrapped in kraft papers, containing 0.002 to 0.003 per cent of active sulphur. As there were no other possible sources of sulphur, all spotting that occurred must have been due to the effect of the papers. A number of articles wrapped in tin foil were also exposed under these conditions at the same time. To test the efficacy of a superimposed film on the lacquer for the prevention of crystal spots, approximately 50 specimens of sulphide finishes were dipped in a 4 per cent solution of petrolatum in C. P. carbon tetrachloride. The surface was then wiped, leaving a transparent film of petrolatum on the lacquered surface. These specimens were then wrapped in kraft paper similar to that employed for wrapping other specimens and exposed under the same conditions and at the same time as the other specimens. The results are shown in Table 3.

TABLE 3.—*Crystal spotting of specimens wrapped with various materials*

[Results after nine months' exposure]

Material employed for wrapping	Humidity	Specimens heavily spotted	Specimens lightly spotted	Specimens unspotted
	Per cent	*Per cent*	*Per cent*	*Per cent*
Kraft paper	90	16	14	70
Do.	30–70	15	21	64
Waxed paper	90			100
Do.	30–70	1		99
Petrolatum film and kraft paper	90			100
Do.	30–70			100
Tin foil	90			100
Do.	30–70			100

By the term "heavily spotted" is meant that the specimens were unfit for commercial use and by "lightly spotted" that only few and small spots were present, which did not unfit the specimen for commercial use.

These results show clearly that wax paper and tin foil are superior to kraft paper. When the latter is used, a petrolatum film is advantageous.

The spots appeared at widely different intervals on the specimens wrapped in kraft paper. Of those specimens which failed spots appeared on about 25 per cent within two weeks, on an additional 40 per cent within six weeks, and on most of the others within three months. The above table also confirms the conclusion (par. 6) that the humidity has no effect upon the rate of spotting.

(5) TEMPERATURE.—Specimens of sulphide finishes in contact with sulphur or rubber were kept at temperatures of 0° to 5° C. (32° to 41° F.); 22° to 27° C. (72° to 81° F.) and 40° to 50° C. (104° to 113° F.), respectively. Very large crystal spots appeared within 12 hours after exposure at the highest temperature; smaller crystal

spots appeared within 2 to 4 days on specimens exposed to room temperatures and within 5 to 7 days on specimens exposed to low temperatures. It is evident from these results that an increase in temperature accelerates the formation of crystal spots on finishes in contact with sulphur. The effect of an increase in temperature may be due to an increase in the vapor pressure of the sulphur, and therefore in its content in the atmosphere, to the acceleration of the process of forming or recrystallizing the copper sulphide, or to an increase in the solubility of sulphur in the lacquer.

(6) HUMIDITY.—As it was commonly believed that high humidity is partly responsible for the formation of these crystal spots, the effect of humidity was determined. The specimens were kept in desiccators with humidities controlled by the concentration of the sulphuric acid present. Samples kept in an atmosphere approaching 90 per cent humidity without any rubber, sulphur, paper, or other accelerating agent present showed at the end of eight months very few spots. It is evident, therefore, that moisture alone does not cause this type of spotting.

When specimens, together with sulphur or rubber, were kept in vessels in atmospheres with zero, 20, 55, and 90 per cent humidities, respectively, the spotting occurred to an equal extent. It is evident, therefore, that the action of the sulphur is not appreciably affected by the humidity.

Specimens wrapped in various kinds of paper were subjected to similar variations in humidity. No differences in the spotting were observed except with cellophane paper which contains more sulphur (0.005 per cent) than any of the other papers used. With this paper a high humidity appeared to increase the tendency toward spotting and also caused tarnishing.

(7) EFFECT OF OXYGEN.—As spots formed occasionally though slowly when no sulphur, rubber, or paper was known to be present, it was thought that the oxygen of the air might contribute to their formation. The fact that on specimens kept in a vacuum in contact with sulphur for 75 days no spots appeared, although tarnishing occurred, seemed to confirm the view that oxygen is necessary. When, however, other specimens and sulphur were kept in pure oxygen and oxygen-free nitrogen, respectively, spotting occurred to an equal extent in each. This shows that oxygen is not necessary and leaves unexplained the results obtained in a vacuum.

3. PLANT TESTS

The elimination of free sulphur or hydrogen sulphide from the atmosphere in contact with the finishes is largely a matter of control of conditions in storage and transit. Sulphur or hydrogen sulphide in the plant atmosphere may come from sulphur-melting furnaces or

from the gases from other types of furnaces. Several well authenticated instances of difficulties arising from vapors from sulphur-melting furnaces being carried to the parts of the plant where sulphide finishes were prepared or stored have been reported. This difficulty was, of course, easily overcome when the source of the trouble was realized.

The danger of the former custom of clipping the wrapped sulphide finishes with rubber bands has been realized, and the practice has been discontinued in a majority of the plants. That such a custom has not been entirely discontinued was emphasized within the past year by the receipt of a shipment of sulphide finishes for experimental purposes clipped with rubber bands and hence spotted when received.

During transit sulphur may come in contact with the finishes in a variety of ways. The danger is especially great during shipments through the Tropics, where the articles may be stored in the hold of steamships and subjected to sulphur gases from coal bunkers and to elevated temperatures. It is obvious that contact with sulphur gases under such conditions might be obviated by shipment in sealed metallic containers if the difficulty experienced warranted the increased expense.

Tests of promising remedies, such as the use of waxed paper and a petrolatum film, were made in four different plants where crystal spotting had been occasionally reported. Approximately 1,000 specimens of oxidized finishes, mainly brass, bronze, and copper-plated steel escutcheon plates, were stored in the four plants under conditions reported to cause spotting. Portions of the lots were wrapped in kraft papers containing the same percentage of sulphur as those employed in laboratory tests and in waxed papers. Others were given a film coating by dipping into a 4 per cent solution of petrolatum in carbon tetrachloride and wiped. The petrolatum film did not discolor or disfigure the specimens. No crystal spotting occurred on any of the specimens after exposures of 8 to 11 months.

Inconclusive results were also obtained from shipments sent out and returned to the plants. One lot of approximately 150 specimens was shipped from Connecticut to Chicago by train and returned after seven months. Another shipment was sent by boat to Australia and returned to this country after seven months. This latter shipment was placed in the hold of the boat in a position neither particularly favorable nor detrimental in respect to sulphur gases. Part of this shipment was placed in hermetically sealed metal boxes instead of the usual wooden packing cases. None of the specimens in any of the shipments showed any crystal spotting. The results of these plant tests indicate the difficulty of obtaining definite results under plant conditions with this type of spotting. They at least indicate that the crystal spotting is much more irregular in occurrence and more

subject to variable conditions of transit and storage than is stain spotting. (No such difficulty was found in obtaining plentiful and definite evidence of the latter in similar plant tests.) It is believed that the following conclusions of the laboratory tests are valid, even though they have not yet been fully confirmed in plant practice. Certainly, whenever plant conditions are such as to cause crystal spotting, the procedures here suggested warrant consideration and trial.

4. CONCLUSIONS

1. Crystal spots appear in the form of dendritic (treelike) crystals on the metal finishes containing copper sulphide, silver sulphide, or nickel sulphide and which are subsequently lacquered.

2. Crystals of the same general structure are encountered in nature under similar conditions of growth; that is, between two planes pressed closely together. Magnetite crystals often grow between flakes of mica.

3. The common crystal spots and the copper sulphide on which they occur both consist of cuprous sulphide, Cu_2S, with the X-ray pattern of the mineral chalcocite.

4. The crystals of cuprous sulphide may conceivably be formed either by a recrystallization of the much finer (but also crystalline) coating produced by the action of polysulphide solutions on copper, or by the formation of new copper sulphide by the slow action of sulphur upon minute areas of copper exposed through the original sulphide film. In the former case the presence of minute amounts of sulphur might simply accelerate the formation of the crystals by a process of recrystallization.

5. The composition of the base metal underlying the coating of copper or brass has no influence on the growth of the crystal spots.

6. Previous treatment of the metal with acids or alkalies does not affect the growth of the crystal spots.

7. The only substance found to accelerate the growth of crystal spots is sulphur, either as free sulphur or as hydrogen sulphide. These may be introduced into the atmosphere either directly or from rubber or paper employed in wrapping the sulphide finishes.

8. An increase in temperature increases the rate of growth of crystal spots in the presence of sulphur.

9. The growth of crystal spots on lacquered sulphide finishes in the presence of sulphur may be retarded by certain types of commercial lacquers. About one-third of the lacquers examined showed distinct value in this respect.

10. An increase in the thickness of the lacquer retards the growth of crystal spots.

11. The employment of waxed papers, in which the sulphur has been rendered inactive by paraffin and which are less permeable

to sulphur vapor or hydrogen sulphide, retards the growth of crystal spots on sulphide finishes.

12. A transparent film of grease or oil on the lacquer film retards the growth of crystal spots in the presence of sulphur.

III. STAIN SPOTTING

1. OCCURRENCE AND COMPOSITION OF STAIN SPOTS

It is common knowledge in the plating industry that far more difficulty is experienced with stain spotting than with the crystal spotting described in the preceding section. The importance of stain spotting is also indicated by the frequent published references to it, especially in the trade publications. Few researches have been conducted upon this subject, and most of the articles, some of which are anonymous, consist of statements regarding its occurrence and possible remedies without giving quantitative data. It is hard, therefore, to judge from such papers the efficacy of the proposed remedies.

In one of the earliest articles [8] it was pointed out that these spots are caused by porosity of the castings and by absorption of liquids in them. Rinsing alternately in hot and cold water was one of the remedies suggested. In an editorial following the above paper the use of sodium salts instead of the more deliquescent potassium salts was suggested.

In the following year [9] suggested remedies included soaking in fish-oil soap, nickel plating before plating with copper or brass, allowing the plated castings to stand and spot out before finishing, and baking after plating. Somewhat later [10] the presence of blisters in the copper deposits was suggested as the cause of spotting.

G. B. Hogaboom on two occasions [11] attributed the spotting to the presence of acid or alkaline materials in the pores and concluded that none of the remedies thus far proposed had proven entirely effective. In fact, he listed this as one of the "unsolved problems in electroplating."

C. F. Burgess and L. T. Richardson [12] studied spotting out on silver plating and concluded that sodium cyanide is more deliquescent than potassium cyanide, and the latter should, therefore, be used.

C. H. Proctor [13] recommended as remedies alternate treatment with hot and cold water and also wrapping in wax paper to exclude moisture.

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[8] Anonymous, Brass World, **2**, p. 369; 1906.
[9] Anonymous, Brass World, **3**, p. 65; 1907.
[10] Anonymous, Brass World, **5**, p. 429; 1909.
[11] Trans. Am. Electrochem. Soc., **19**, p. 53; 1911; **29**, p. 376; 1916
[12] Metal Ind., **11**, pp. 477 and 508; 1913.
[13] Metal Ind., **12**, p. 281; 1914.

Remedies suggested by F. Ottman [14] included boiling in cream of tartar solution and dipping in nickel or acid copper solutions in order to neutralize alkalis in the pores.

R. M. Goodsell [15] advocated as remedies the presence of sufficient free cyanide in the plating bath, thorough rinsing, baking before lacquering, and the application of the water-dip lacquer when the articles are cold.

In a more recent article C. H. Proctor [16] advised the maintenance of a low content of free cyanide in the plating solution, rinsing in hot and cold water, baking at 212° F. (100° C.), and the application of water-dip lacquers at a temperature of 120° F. (49° C.).

A. K. Graham [17] found that the pores are not necessarily present in the original castings but may be caused by the attack of cleaning or pickling solutions upon segregated impurities in the castings. He therefore emphasized the importance of producing castings that are free not only of pores but also of segregations.

From a study of the literature and from preliminary observations in plants and in the laboratory the following tentative conclusions were reached regarding the occurrence, cause, and nature of stain spots:

1. Stain spots may occur on either oxidized or unoxidized finishes.
2. Stain spots occur on both lacquered and unlacquered specimens, while crystal spots occur only on lacquered objects.
3. Stain spots occur on both plated and unplated castings.
4. Moisture in the surrounding atmosphere is necessary to produce stain spots. Specimens that were exposed for several weeks at zero humidity without staining spotted badly in a few hours upon removal to an atmosphere with high humidity.
5. Stain spots usually occur in a humid atmosphere in a few hours, while crystal spots may not appear under normal conditions of storage until weeks or months after finishing.
6. Stain spots are associated with pores in the casting, either present originally or produced by the action of various solutions. This conclusion is drawn from the frequent presence of a small dark spot in the center of each stain and from the fact that in many cases stains reappear at the same points when the stained specimens are stripped and polished to a new metal surface and then replated and refinished. The stains frequently reappear at the same points after two or more refinishing operations. These observations confirm those made by A. K. Graham and others.

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[14] Metal Ind., **14**, p. 153; 1916.
[15] Month. Rev. Am. Electroplaters' Soc., **12**, p. 16; Sept. 1, 1925.
[16] Metal Ind., **24**, p. 370; 1926.
[17] Month. Rev. Am. Electroplaters' Soc., **14**, p. 4; March, 1927

7. The stains involve the presence of "hygroscopic" (moisture absorbing) compounds occluded or formed in the pores of the metal by the action of cleaning, plating, or coloring solutions.

8. Either alkaline or acid compounds may cause stain spotting. Alkaline materials are, however, more likely to be retained in the pores, even when both acid and alkaline solutions have been applied to the metals. Definite evidence of this was furnished by the fact that the phenol-condensation lacquers subsequently applied are turned pink adjacent to the spots. This reaction is characteristic of the action of alkalis on phenol-condensation products.

9. Moisture in the atmosphere absorbed by salts in the pores of a metal may cause the salts to "creep" out over the surface, producing a stain and in extreme cases a crystallization of solid material on the surface of the object within the area of the stain.

10. It is also possible for stains to form on metals which are not porous by the evaporation on their surface of contaminated rinse waters, leaving compounds which attack and discolor the surface. As this type of spotting can be completely and conveniently prevented by more thorough rinsing in clean water, no actual investigation of other remedies was necessary.

2. FACTORS INVOLVED

(a) METHOD OF TEST EMPLOYED

In order to obtain comparative results within short periods, an accelerated test for stain spots was employed. This consisted simply in exposing the articles at 20° to 30° C. (68° to 86° F.) to a high humidity (90 to 100 per cent) in a closed vessel containing water. Under such conditions the stain spotting usually appears in a relatively short time.

(b) THE BASE METAL

If porosity of the base metal is responsible for the retention of solutions and their subsequent staining of the surface, the most obvious remedy would be to employ only castings free from pores. It is at least possible that less porous castings might be made by changing the foundry conditions, such as the composition or temperature of the molten metal, the design of the patterns, or the character of the molds. Experimental work upon such possibilities must be conducted in a foundry, as it is difficult to reproduce foundry conditions in small-scale laboratory experiments. That such possibilities at least deserve investigation is indicated by the experience of one plant. A simple change in the design of a cast-iron flush-bolt case, resulting in a thicker average cross section, made a marked decrease in the tendency to spot. Laboratory tests on these products showed that, after being brass plated and lacquered, 100 per cent of

the thin-walled samples failed in the humidity test and only 15 per cent of the thick-walled. Similar differences were observed in plant experience with these products. Metallographic cross sections of the two products failed, however, to show any significant difference in the structure or porosity of the castings. This subject needs further study.

When it is not feasible to change the pattern, it is sometimes possible to select a less porous metal. Thus, in one plant the spotting was overcome by substituting rolled steel for malleable iron in lock fronts that were subsequently brass plated.

(c) CLEANING AND PLATING PROCESSES

If, as was indicated by the preliminary studies, alkaline solutions are most likely to be absorbed and retained in the pores, it would naturally be desirable to eliminate such materials from the process. Actually, however, alkaline solutions, such as those of sodium hydroxide, carbonate, and phosphate, are commonly used for cleaning metals to remove grease and similar foreign materials, and alkaline cyanide copper and brass solutions are used in most of the plating processes. It is not feasible to substitute other methods or materials for the alkaline cleaning operations. Scrubbing with pumice or similar materials may completely remove grease but is expensive and inconvenient. On iron and steel acid copper solutions can not be used directly for plating, and there is no practical acid brass plating solution. It is obvious, therefore, that for most purposes alkaline solutions will be found necessary. When brass parts are copper plated for subsequent "oxidizing" with polysulphides, acid copper baths may be substituted for the cyanide copper commonly used. It is also possible to use instead of potassium or sodium polysulphide a solution of ammonium polysulphide, which is less likely to leave nonvolatile alkaline compounds in the pores.

In order to determine whether by elimination of sodium or potassium salts, the stain spotting can be reduced, the following experiments were made. A number (lot 1) of cast brass and bronze parts were cleaned electrolytically in an alkaline solution, plated in a copper cyanide solution, colored with potassium polysulphide, and lacquered. Others (lot 2) of the specimens were cleaned by pumice scrubbing, plated in an acid copper bath, colored with ammonium polysulphide, and lacquered. The specimens were then placed in the humidity chamber. Within 12 hours 68 per cent of lot 1 were badly spotted, and at the end of 63 days only 8 per cent were unspotted. Of lot 2, 16 per cent spotted badly in from 1 to 7 days, but at the end of 63 days the remaining 84 per cent were unspotted. No similar improvement was noted when electrolytic cleaning instead of pumice scrubbing was used in the procedure employed for lot 2. Evidently,

therefore, introduction into a strong alkaline solution at any stage is detrimental. The concentration of alkali in the polysulphide solutions used for coloring (less than 0.05 *N*) is small, and no detectable effect was obtained by substituting ammonium polysulphide for the potassium compound.

In finishing certain classes of work, especially solid brass or bronze, it is sometimes possible to obtain the desired appearance by means of "greaseless polishing compounds." Their use eliminates the necessity of subsequent washing or cleaning processes to remove grease and abrasives left from the polishing operation. This procedure avoids the possibility of alkaline liquids entering the pores and producing spots.

(d) REMOVAL OR EXCLUSION OF COMPOUNDS FROM THE PORES

The permanent presence of the objectionable alkaline salts in the pores might be prevented by excluding, neutralizing, or removing them.

Attempts to first fill the pores with some viscous inert substance, such as glycerin or lacquer, that might prevent access of the alkaline cleaning or plating solutions into the pores were unsuccessful. Attempts to first fill the pores with a neutral or acid solution were also unsuccessful. Plating in a nickel bath before introducing into any alkaline solution produced no improvement. Boiling gray-iron castings with dilute chromic acid (25 g/l or 3.3 oz./gal., CrO_3) before cleaning or plating was also ineffective.

Treatment of the plated castings with acid solutions, such as acetic acid (50 g/l or 6.7 oz./gal.), chromic acid (25 g/l or 3.3 oz./gal.), hydrochloric, sulphuric, or nitric acid (30 g/l or 4 oz./gal.), and cream of tartar (6 g/l or 0.8 oz./gal.), each followed by thorough rinsing, all failed to prevent the subsequent spotting. Actually many of these acid rinses attacked and discolored the plated coatings.

Extended rinsing with either hot or cold water or alternately with hot and cold water had no appreciable effect on the spotting. All these experiences indicate that the pores in the metal must be very fine capillaries, and also that alkaline solutions are much more strongly held in such pores than are acid solutions.

Baking the plated parts to about 225° F. (107° C.) before lacquering dehydrates any compounds in the pores and retards the tendency to spot. This procedure is not applicable, however, in many plant procedures or to metals with a sulphide finish, which discolors at temperatures above about 60° C. (140° F.).

No improvement was obtained by plating with thicker deposits or by plating with several coats of copper or brass. It is evident, therefore, that the pores are not filled up or sealed up by metal.

Mechanical operations, such as burnishing and tumbling after plating, were found to produce a slight improvement, which indicates that some of the pores were at least partially sealed up. This procedure is not, however, applicable to all products.

The only practicable method of reducing the concentration of the deliquescent alkaline compounds in the pores is to expose the articles to a high humidity for 12 to 24 hours, under which conditions a large part of the salts exude, and, of course, produce stains on the surface. These can then be removed by scratch brushing or buffing and the articles finished and lacquered. Even this procedure is not effective if the castings are very porous. It is, however, valuable in decreasing the content in the pores of alkali which may subsequently absorb moisture and attack the lacquer. Thus, in one series of experiments it was found that such preliminary spotting increased from 5 to 25 per cent the proportion of unstained castings that were subsequently coated with a poor lacquer. With similar specimens from the same lot of castings coated with two better lacquers the preliminary spotting increased the yield of unspotted samples from 70 to 100 per cent and 45 to 75 per cent, respectively.

(e) THE PROTECTIVE COATING

If it were feasible to keep the finished articles in a practically dry atmosphere, no stain spotting would occur. This is, of course, not practicable, though it is often possible to avoid storage of such products in rooms with high humidity.

It is necessary, therefore, to depend upon a coating, such as lacquer, to prevent access of moisture. Preliminary experiments showed that phenol-condensation lacquers were more efficient in preventing stain spotting than were the average nitrocellulose lacquers. Thus, with brass and bronze castings from the same lot that had been copper plated in a copper cyanide solution and colored with polysulphides, phenol lacquers prevented any spotting within two weeks, while with one nitrocellulose lacquer 75 per cent were spotted and with another 25 per cent. Very similar ratios were obtained with these lacquers on brass-plated gray iron and malleable iron castings. As it was known from previous studies on the waterproofing properties of lacquers that the phenol products were relatively impervious to moisture, their value against stain spotting was naturally attributed to this property. The relative permeabilities of different lacquer films to moisture were determined by the following method, which is based on that described by P. H. Walker and E. F. Hickson[18] for testing paint coatings:

A circular hole about 5 cm (2 inches) in diameter was cut in the cover of a tinned iron box (a common ointment box) and a piece of

[18] B. S. Jour. Research, 1 (RP1), p. 1; 1928.

100-mesh copper gauze was soldered across the opening. To this gauze were then applied several coats of the lacquer to be tested until a definite increase in weight, corresponding to an arbitrary film thickness, was obtained. Each coat was dried by the method adapted to the lacquer used. The cover was then put on the box in which had been placed about 5 g of anhydrous calcium chloride. The joint was sealed with paraffin and the box was weighed, placed in the high humidity chamber, and reweighed at intervals. The gain in weight indicated the permeability of the lacquer to water vapor. Blank tests were also run without any calcium chloride in the box to measure the tendency of the lacquer to adsorb moisture. The freedom of the films from microscopic pores was proven by testing their resistance to the passage of air when the pressure was reduced on one side.

These tests (reported in Table 4) showed conclusively that the phenol-condensation lacquers, which are very effective against stain spotting, are more impervious to moisture than are nitrocellulose lacquers. (The phenol lacquers, however, adsorb more moisture than the nitrocellulose.) When the same test was applied to different lacquers containing nitrocellulose, it was found that some samples which are relatively permeable to moisture, exert more protection against stain spotting than other samples with lower moisture permeability. This is illustrated in Table 4 in which the lacquers have the same numbers as in Table 5.

TABLE 4.—*Permeability of lacquer films to moisture*

[Exposed to high humidity at about 25° C. (77° F.) for 14 days]

Lot No.	Lacquer type	Total gain in weight	Gain in weight of lacquer film	Gain in weight of $CaCl_2$= weight H_2O passed through lacquer film
		g	g	g
1	Phenol condensation	0.0222	0.0087	0.0135
2	Not designated	.1789	.0032	.1757
3	Nitrocellulose	.1024	.0026	.0998

The rate of moisture absorption and stain spotting does not decrease appreciably with a considerable increase in the thickness of the lacquer film. Thus, when the film thicknesses of lacquers (2 and 3, Table 4) were increased 100 per cent there was only a 10 per cent reduction in the permeability to moisture. An increase of 100 per cent in the thickness of a single lacquer film on specimens coated with these lacquers caused no noticeable decrease in the amount or rate of stain spotting. It is evident from Tables 4 and 5 that even though impermeability to moisture is a highly desirable property of a lacquer to resist stain spotting, it is not the only useful property.

Others may include improved adherence, resistance of the lacquer film to attack by compounds in the pores, or ability to form with such compounds substances which seal the pores or are impermeable.

As the quality of the lacquer had been found to have so great an effect on stain spotting, numerous samples of commercial and experimental lacquers (also tested for crystal spotting) were compared by the following method:

Test for stain spotting of brass plated gray iron castings.—A large number of pieces of a type known to be subject to stain spotting, preferably cast in the same lot, are sampled after the customary machining and polishing. At least 10 and preferably 25 specimens are selected at random for each set of experiments. They are then treated as follows:

1. Clean electrolytically as cathode for three minutes in a solution containing 60 g/l (8 oz./gal.) of sodium carbonate, 7.5 g/l (1 oz./gal.) of sodium cyanide, and 7.5 g/l (1 oz./gal.) sodium hydroxide at 60° C. (140° F.), and rinse in warm water.

2. Pickle for about one minute in hydrochloric acid (1 part concentrated hydrochloric acid to 2 parts by volume of water) and rinse in cold water.

3. Clean electrolytically for one minute as in 1.

4. Brass plate at room temperature for 40 minutes at approximately 0.3 amp/dm ^{2} (3 amp/sq. ft.) in a regular brass plating solution; for example, one containing—

Copper cyanide, CuCN	19	g/l (2. 5 oz./gal.)
Zinc cyanide, $Zn(CN)_2$	8	g/l (1. 1 oz./gal.)
Sodium cyanide, NaCN	34	g/l (4. 5 oz./gal.)
Sodium carbonate, Na_2CO_3	7. 5	g/l (1 oz./gal.)
Ammonium hydroxide (sp. gr. 0.90)	1	cc/l (0. 15 fl. oz./gal.)

5. Rinse the specimens in hot water, allow to dry in the air, and store them for 24 hours in an atmosphere with high humidity (for example, in a closed space containing an open vessel of water) in order to permit them to spot out. (This step has been found to be the most effective mans of removing excessive amounts of the chemicals from the pores, which would otherwise destroy the lacquers. It may be omitted if the castings are not extremely porous. All comparable tests should be made under the same conditions.)

6. Scratchbrush the articles with pumice and water to remove the stains and to produce a dull brass finish, rinse, and dry.

7. Dip into lacquer, allow the coating to dry, and apply baking or other treatment suitable to the lacquer employed. In order to produce lacquer films of approximately equal thickness, dilute the lacquer with thinner until it just produces an iridescent film on a dipped metal specimen. Then add just enough lacquer to prevent the formation of this iridescence.

8. Expose the articles to a high humidity at 20° to 30° C. (68° to 86° F.); for example, over water in a closed vessel. Examine the samples at the end of 2, 4, and 24 hours, and every 24 hours thereafter for a week, and note the number and extent of the spots.

The castings employed were taken at random from a lot of 600 gray iron "catch cases." In each experiment 10 castings were used, and each lacquer was tested with two lots of 10 each, prepared on different days. The average of the 20 samples are reported in Table 5. By "badly spotted" is meant conspicuous or numerous spots. "Lightly-spotted" samples are those on which the spots are noticeable but not conspicuous. The total spotting, that is, the sum of the two preceding columns—represents the proportion that would probably be rejected by a careful inspection.

TABLE 5.—*Effects of lacquers on stain spotting*

[Exposed to high humidity for 1 week]

Lot No.	Lacquer type (as designated by manufacturer)	Temperature of baking		First appearance of spots days	Condition after one week		
		°C.	°F.		Badly spotted	Lightly spotted	Total spotted
					Per cent	*Per cent*	*Per cent*
	GROUP I						
1	Phenol-condensation resin	135	275	2	20	0	20
4	Not designated	50	122	1	5	10	15
6	do	50	122	6	0	10	10
8	do	50	122	4	0	10	10
9	do	50	122	1	15	5	20
12	do	50	122	1	15	5	20
15	Phenol-condensation resin	135	275	3	5	0	5
18	Not designated	50	122	1	15	10	25
24	do	135	275	1	10	10	20
	GROUP II						
2	Not designated	50	122	1	15	25	40
14	Synthetic gum	50	122	1	20	25	45
17	Not designated	50	122	1	15	25	40
19	do	50	122	1	15	30	45
20	do	50	122	1	20	30	50
22	do	50	122	1	30	10	40
	GROUP III						
3	Nitrocellulose	50	122	[1] 1	45	20	65
5	Not designated	50	122	[1] 1	45	35	80
7	Nitrocellulose and natural resin	50	122	[1] 1	45	30	75
10	Nitrocellulose and gum	50	122	[1] 1	75	15	90
11	Not designated	50	122	[1] 1	25	40	65
13	Nitrocellulose and natural resin	50	122	[1] 1	90	10	100
16	Synthetic resin	50	122	[1] 1	15	40	55
21	Not designated	50	122	[1] 1	70	5	75
23	do	50	122	[1] 1	70	20	90

[1] Less than one day.

In Table 5 these lacquers have been divided into three groups. Group I contains those with which less than 25 per cent of the samples spotted, Group II those with 25 to 50 per cent spotted, and Group III those with over 50 per cent spotted.

Owing to the limited time available, only a few of the lacquers tested in Table 5 have been used in extended laboratory and plant tests. These results are therefore chiefly of value in showing the importance of lacquers in connection with stain spotting and the possibility of developing or selecting the most suitable lacquers for this purpose. Further tests should, therefore, be made by the makers and users of these lacquers. Before adopting any lacquer for commercial work its suitability should be determined by such tests as are described in this paper. In addition, it is necessary in each case to determine by appropriate tests whether the lacquer possesses other qualities essential for a given class of work, such as color, flexibility, and resistance to the effects of light, weathering, and abrasion.

It may be noted by comparing Tables 1 and 5, that a given lacquer is not necessarily or usually suitable for preventing both types of spotting. Only two samples (6 and 9) were in Group I for each purpose. When otherwise suitable, such a lacquer is desirable for use on castings having a sulphide finish.

(f) THE ENVIRONMENT

As previously noted, the only constituent of the atmosphere that contributes directly to the stain spotting is the moisture, the absorption of which causes compounds present in the pores to exude. Other substances, such as carbon dioxide and sulphur compounds, may change or affect the color and character of the spots but not their occurrence. The temperature of the air is chiefly of importance to the extent that changes in temperature affect the relative humidity. Thus, a sudden decrease in temperature of a humid atmosphere may bring it to the dew point and cause actual condensation of moisture on the surface, and thus accelerate spotting.

3. PLANT TESTS

Observations were made in four different plants upon the behavior of large lots (from 100 to 300 each) of castings prepared by definite procedures. At the time when these tests were made—that is, in September and October, 1928—the extended laboratory tests on lacquers had not been completed. Only a few of these lacquers were, therefore, tested in the plants. To be conclusive, the plant tests must be made when conditions are favorable for spotting, preferably in the humid summer months. The results of the plant tests are valuable chiefly for showing that with different lacquers or different methods of operation results are obtained which are similar and parallel to the results of laboratory tests. By such confirmations they add weight to the results obtained in the laboratory.

(a) GRAY IRON CASTINGS

A lot of 300 window catches and cupboard turns were machined and polished, cleaned anodically in dilute potash, pickled in 2 : 1 hydrochloric acid, dipped in a weak sodium cyanide solution, cleaned as cathodes in alkali, and brass plated.

These were divided into four lots and finished as follows:

Lot 1. Wet scratch-brushed with pumice, dried and dip lacquered in a nitrocellulose lacquer, and dried at 40° to 50° C.

Lot 2. As in lot 1, but dipped in a phenol-condensation lacquer, baked at 135° C. (275° F.).

Lot 3. Allowed to spot out for three days and then finished as in lot 1.

Lot 4. Allowed to spot out for three days and then finished as in lot 2.

The samples were then exposed to the air in the lacquer room. The results shown in Table 6 show clearly the superiority of the phenol-condensation lacquer. With this lacquer it was beneficial to allow the specimens to spot before finishing, but with the nitrocellulose lacquer practically all the specimens spotted in a few hours, even when they had been allowed to spot previously, although in the latter case the intensity and extent of the stain spotting were reduced.

TABLE 6.—*Spotting of brass-plated gray iron*

Lot No.	Finished	Lacquer	Badly spotted		
			12 hours	10 days	20 days
			Per cent	*Per cent*	*Per cent*
1	Immediately	Nitrocellulose	100	100	100
2	do	Phenol-condensation	0	33	33
3	After 3 days	Nitrocellulose	97	97	97
4	do	Phenol-condensation	0	0	0

(b) BRASS AND BRONZE

Cast-brass and bronze escutcheon plates were dipped in a mixture of equal parts of concentrated nitric and sulphuric acids and rinsed, machined and polished, cleaned in gasoline, dipped in concentrated sulphuric acid and rinsed, dried, scratch brushed, treated with potassium polysulphide, scratch brushed, and relieved.

The brass and bronze specimens were each divided into two lots. Lot 1 of each was dipped in nitrocellulose lacquer and baked at 105° C. (221° F.) for 45 minutes and lot 2 in phenol-condensation lacquer and similarly baked. They were then exposed to the air in the lacquer room. The results, as shown in Table 7, again show the difference in the values of the two types of lacquers.

TABLE 7.—*Stain spotting of brass and bronze castings*

Lot No.	Metal	Lacquer	Spotted		Badly spotted, 16 days
			12 hours	16 days	
			Per cent	*Per cent*	*Per cent*
1	Brass	Nitrocellulose	85	100	65
2	do	Phenol-condensation	0	38	13
1	Bronze	Nitrocellulose	85	100	64
2	do	Phenol-condensation	0	0	0

(c) MALLEABLE CAST IRON

About 100 malleable-iron castings were machined and polished, cleaned cathodically in alkali, plated with a very thin copper coat from cyanide bath, brass plated, allowed to spot for 24 hours, and scratch brushed.

One-half were then coated with nitrocellulose and one-half with phenol-condensation lacquer. No numerical data were reported, but the statement was made that the phenol-condensation lacquer greatly reduced the spotting.

(d) REFINISHED CASTINGS

In another plant a large number of brass, bronze, and cast-iron pieces, each of which had been previously finished by the usual procedure, including a nitrocellulose lacquer, and had spotted badly, were refinished by the same process, except that three different lacquers were used. The results of exposure to the plant atmosphere were as shown in Table 8.

TABLE 8.—*Stain spotting of refinished articles*

Metal	Lacquer	Badly spotted	
		24 hours	10 weeks
		Per cent	*Per cent*
Brass and bronze	Phenol-condensation	20	60
Do	Nitrocellulose	100	100
Do	do	54	70
Cast iron, 1	Phenol-condensation	0	0
Do	Nitrocellulose	90	90
Do	do	0	10
Cast iron, 2	Phenol-condensation	0	25
Do	Notrocellulose	90	90
Do	do	50	80

These results are especially significant because they show that even on specimens known to be so porous as to have spotted badly the phenol-condensation lacquers are somewhat superior to the nitrocellulose.

4. CONCLUSIONS

1. Stain spots occur on both lacquered and unlacquered specimens.
2. Stain spots occur on either oxidized or unoxidized finishes.
3. Stain spots occur on both plated and unplated materials.
4. Stain spots usually involve at least three factors—(*a*) porosity of the metal; (*b*) the presence in the pores of hygroscopic (moisture absorbing) compounds occluded or formed by the action of alkaline

or acid cleaning, plating, or coloring solutions; and (*c*) the absorption of moisture by the compounds in the pores. This may cause the salts to "creep" out over the surface, producing a stain and in extreme cases a crystallization of solid material on the surface of the object within the area of the stain.

5. Stain spotting usually occurs under humid conditions within a few hours or at most a few days, depending on the type of lacquer film employed.

6. The amount of stain spotting may be reduced by using a less porous base metal.

7. Stain spotting may be slightly reduced on plated materials by burnishing the surface; that is, by dry barrel tumbling or rolling.

8. While stain spotting may be reduced under certain conditions by the elimination of alkaline cleaning or plating solutions from the procedure, this expedient is very seldom practical in plant operations.

9. Stain spotting may be reduced by allowing the articles to spot out for 24 hours or more prior to the final finishing and lacquering.

10. The best general remedy for the reduction of stain spotting is the use of satisfactory lacquer films.

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WASHINGTON, March 9, 1929.

THE ARC SPECTRUM OF CHLORINE AND ITS STRUCTURE

By C. C. Kiess and T. L. deBruin

ABSTRACT

In the arc spectrum of Cl, emitted by an uncondensed discharge in a Geissler tube containing the gas at low pressure, more than 200 wave lengths were measured between the limits 4000 A in the violet and 9900 A in the infra-red. Sixty-two per cent of these lines, together with those observed by Turner in the Schumann region, have been classified as resulting from combinations between terms of the doublet and quartet systems. These terms arise mainly from the basic term ^3P of the ion, the terms coming from ^1S and ^1D not being definitely established, owing to the faintness of the lines. Nine sets of series-forming terms have been found. From these, the distance separating $^2P_2$, the base term of the neutral atom, from $^3P_2$, the lowest term of Cl^+, is found to be 104,991 cm^{-1}, giving 12.96 volts as the ionization potential of neutral chlorine.

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I. INTRODUCTION

In discussing the spectra of chlorine Kayser lists 114 papers dealing with this element in Volumes V and VII of the Handbuch. In Volume V, his summary of our knowledge of the chlorine spectra is: "Trotz mancher Untersuchungen ist das Spektrum des Chlors noch recht unbekannt." This estimate was changed but little on the appearance, in 1924, of Volume VII, which gives the wave-length measurements of Exner and Haschek.[1] Since this work was completed, however, several papers have appeared which have greatly extended our knowledge of the spectra, especially in the ultra-violet, and beyond. These are by (1) Jevons,[2] who gives the wave lengths in I. A. of about 200 lines between the limits 3354 A and 2070 A; (2) Angerer,[3] whose work covers approximately the same region and is in good agreement with that of Jevons, although each author gives some lines not observed by the other; (3) Millikan and Bowen,[4] who

[1] Die Spektren der Elemente bei normalem Druck, **III**, 1912. Franz Deuticke, Leipzig und Wien.
[2] Proc. Royal Soc. (London), A 103, p. 193; 1923.
[3] Zeit. für wiss. Phot., **22**, p. 200; 1924.
[4] Phys. Rev., **25**, p. 600; 1925.

for the first time present wave lengths in the extreme ultra-violet; (4) L. and E. Bloch,[5] who describe a method for separating the spectra according to the degree of ionization of the emitting particle; (5) Turner,[6] who presents seven lines characteristic of the arc spectrum lying in the Schumann region; (6) L. and E. Bloch,[7] whose earlier results are here extended to cover the region from 6850 A to 2202 A and consist mainly of lines belonging to Cl II and Cl III; (7) Vaudet,[8] whose wave lengths characterize various stages of spark spectra and extend the results of the Blochs from 2252 A to 1298 A; and (8) Bowen,[9] who gives new wave-length measurements of lines lying in the far ultra-violet and a classification of lines characteristic of Cl II, Cl III, Cl IV, and Cl V.

In addition to these papers, describing hitherto unexplored regions of the spectrum, two other papers, one by Lunt,[10] the other by Asagoe,[11] describe the effect on the wave lengths of varying conditions of excitation. As a result of his studies Asagoe was able to distinguish three types of lines which he correctly interpreted as characteristic of the arc and spark spectra of chlorine.

II. EXPERIMENTAL PROCEDURE

At various times since September, 1922, the chlorine spectrum has been photographed at the Bureau of Standards for the purpose of extending our knowledge of the region of longer wave length. The work owed its inception to the appearance of many unknown lines on a spectrogram of an oxygen-filled Geissler tube obtained a year previously. The oxygen had been generated by heating a small amount of potassium perchlorate in a side tube attached to the discharge tube. These new lines, unidentifiable with any lines known at that time, were suspected as being due to chlorine, a suspicion subsequently proved correct.

In the present work the source employed for the chlorine exposures was a Geissler tube attached to a reservoir containing dry chlorine. Figure 1 is a schematic representation of the apparatus. The chlorine was generated by heating with a Bunsen flame dry auric chloride in the side tube *A*. The gas passed into the reservoir *B*, where it was dried over P_2O_5. From this bulb it could be admitted to the discharge tube *C* as needed. Owing to the rapid disappearance of the Cl within the discharge tube through combination with the metal of the electrodes, it was necessary at frequent intervals to replenish the

[5] Compt. Rend., **180**, p. 1740; 1925.
[6] Phys. Rev., **27**, p. 397; 1926.
[7] Ann. de Phys., **8**, p. 397; 1927.
[8] Compt. Rend., **185**, p. 1270; 1927.
[9] Phys. Rev., **31**, p. 34; 1928.
[10] Monthly Notices, Roy. Astron. Soc. **85**, p. 148; 1924.
[11] Mem. College Sci. Kyoto Imperial Univ., **10**, p. 15; 1926.

gas within the tube from the reserve supply in the bulb *B*. When a tube had been in operation for several hours, a stage was reached approaching saturation, after which it would be necessary to admit gas from the reservoir only every three of four hours. But by this time the capillary was usually incrusted with a semitransparent film which greatly dimimished the intensity of the light. Tubes were made either of pyrex or of fused quartz, the electrodes being disks of platinum 1 cm. in diameter and a millimeter in thickness.

For the earlier series of observations the tubes were excited by a transformer which stepped up 100 volts a. c. to 10,000 volts. For the final series of observations a 40,000-volt transformer was used. Visual observations of the tubes, made with direct-vision spectro-

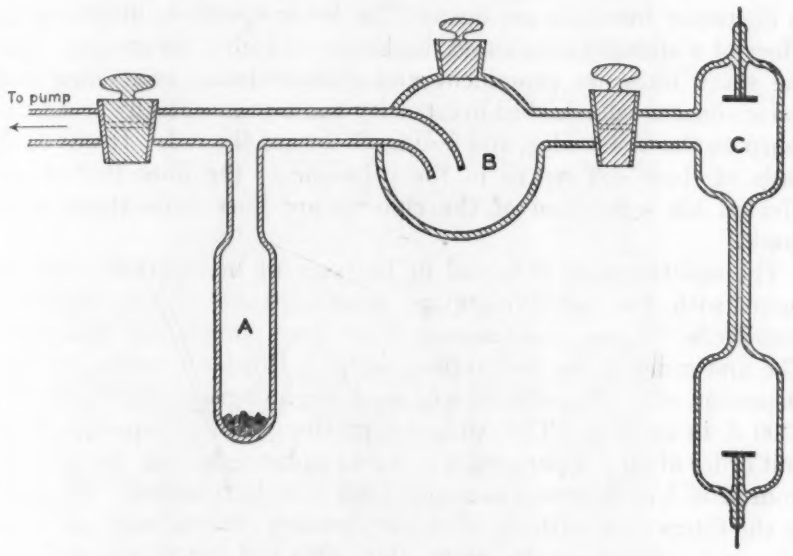

FIGURE 1.—*Chlorine generator and discharge tube used in studying the spectra of Cl.*

scopes, showed that the type of spectrum obtained depended both on the nature of the discharge and on the gas pressure within the tube. When an uncondensed discharge passed through the tube, with the gas pressure estimated under 20 mm Hg, the visual spectrum consisted of but few lines superposed on a background of faint continuous light, the color of the light in the capillary being pale red. If now the pressure of the gas was increased to 50 mm or more, many new lines, quite sharp and brilliant, appeared, the color of the capillary becoming grayish blue. Introduction of capacity of 0.006 μf caused the first type of lines to weaken and disappear in the faint continuous background; the lines of the second type became broadened and diffuse, while a third type of lines, sharp and brilliant,

appeared. These observations are in accord with those reported by previous observers, notably Eder and Valenta,[12] Goldstein,[13] Nelthorpe,[14] and Asagoe.[15] We now know that these various types of lines are characteristic of the neutral and ionized stages of the chlorine atom.

Most of the spectrograms obtained in this investigation show at least two types of lines, since it was impossible to maintain, during the time necessary to make an exposure, the conditions favorable for the excitation of but one type. In Figure 2 is shown a portion of the spectrum extending from 4300 A to 4680 A. The upper spectrum was obtained with the uncondensed discharge in the gas at low pressure. This is the condition favorable for the excitation of the arc lines, a few of the more intense spark lines appearing, but indistinguishable in character from the arc lines. The lower spectrum illustrates the effect of a strongly condensed discharge on high-pressure gas. Here the spark lines are prominent and symmetrically broadened while the arc lines are diminished in intensity and asymmetrically broadened, sharp on the violet edge, and fading off toward the red. It was on the basis of these differences in the behavior of the lines that Asagoe effected his separation of the chlorine arc lines from those of the spark.

The spectrograms obtained in the present investigation were secured with the concave-grating spectrographs of the Bureau of Standards. These instruments have been frequently described.[16] The first order of the 20,000 lines per inch Rowland grating, giving a dispersion of 3.9 A per mm, was used to photograph the region from 2300 A to 5600 A. The Anderson grating, with a dispersion in the first order of 10.4 A per mm, was used in photographing the spectrum from 5200 A in the green to nearly 9900 A in the infra-red. Inasmuch as the filters used with the Anderson grating covered only half of the slit, each of the spectrograms thus obtained contained the overlapping second order in addition to the first-order spectrum. In all the observations the iron-arc spectrum was photographed to furnish the reference standards.

The earlier series of spectrograms were photographed on flat plates 20.5 cm long by 6.5 cm wide and coated with Seed 30 emulsion. For the later series of observations, both with the Rowland and with the Anderson gratings, either Schleussner ultra-rapid or Eastman 36 plates were used. These were 40 cm long by 6 cm wide and were on extra-thin glass so that they could be bent to fit the focal curves of the spectrographs. To render the plates sensitive to the green,

[12] Beiträge zur Photochemie und Spektralanalyse, pp. 358–368; 1924, Wien.
[13] Astrophys. J., 27, p. 25; 1908.
[14] Astrophys. J., 41, p. 16; 1915.
[15] See footnote 11, p. 1118.
[16] B. S. Sci. Papers Nos. 312, 441, and 499.

FIGURE 2.—*Arc and spark spectra of chlorine in the violet and blue*

a, Uncondensed discharge in gas at low pressure; *b*, condensed discharge in gas at high pressure

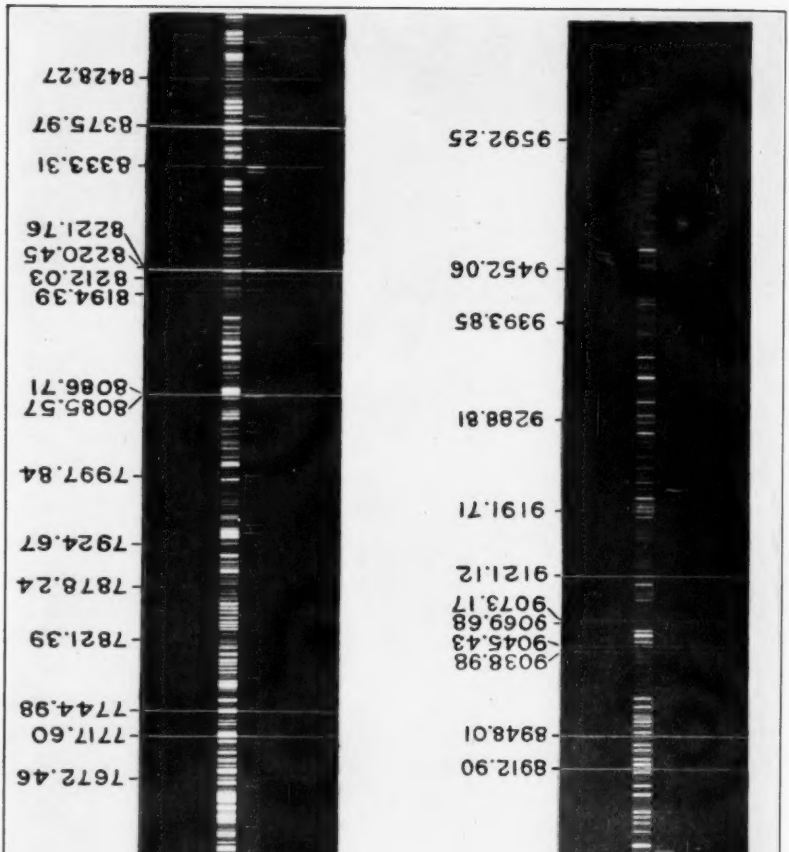

FIGURE 3.—*Arc spectrum of chlorine in the red and infra-red. First and second order Fe arc comparison spectrum*

yellow, red, and infra-red portions of the spectrum, they were bathed in solutions of pinaverdol, pinacyanol, dicyanin, and neocyanin, respectively, by the well-known methods.[17] The 40 cm plates when used with the Anderson grating cover a range of 4000 A in the first order. When these plates were used in photographing the region from 6400 A to 10000 A it was found that the following dye bath proved excellent in rendering them "panchromatic":

	ml
Water-alcohol mixture (85 parts H_2O+60 parts C_2H_5OH)	150. 0
Neocyanin solution (1:2000 in C_2H_5OH)	1. 5
Rubrocyanin solution (1:1000 in C_2H_5OH)	2. 0
Dicyanin solution (1:1000 in C_2H_5OH)	2. 5
Strong ammonia water	5. 0

The plate is soaked for five minutes in this bath and then rinsed for half a minute in alcohol, after which it is rapidly dried in a current of air. The plate from which Figure 3 was made was sensitized by this method. The uniformity of the sensitization can be judged from the exposure to the iron arc in the first order, which lasted five minutes and, on the original negative, can be followed to the line at 9307 A. The exposure times required to record the chlorine spectra ranged from a few minutes for the spark lines in the blue and violet to 15 hours for the infra-red arc lines.

III. RESULTS

The wave lengths derived from measurement of the spectrograms are given in the first column of Table 1. The majority of these wave lengths represent mean values obtained from 3 to 12 determinations, their relative accuracies being indicated by the letters in the third column, which have the following significance:

A = probable error of 0.000 A to 0.01 A.
B = probable error of 0.01 A to 0.02 A.
C = probable error of 0.02 A to 0.03 A.
D = probable error greater than 0.03 A.
E = only one determination.

Lines measured only once have been corrected by an amount necessary to reduce the other wave lengths of the same spectrogram to the mean of all the measurements. It is believed that all the lines listed in Table 1 are, with a few exceptions, characteristic of the neutral Cl atom. The doubtful lines appear to belong to iodine, and there is a possibility that some of the fainter lines may belong to the spectrum of Cl^+.

In addition to a few lines of silicon and the Balmer lines of hydrogen, the impurity lines which appeared on the spectrograms originated with the metals used for the lead-in wires of the Geissler tubes. In the quartz tubes these wires, to which the Pt electrodes were attached,

[17] B. S. Sci. Paper No. 422.

were of molybdenum; and in the pyrex tubes, they were of tungsten. On the earlier spectrograms, lines of either Mo or W were prominent according to the tube used. In the later work, in which new tubes were employed, the precaution was taken of shielding the lead-in wires from the chlorine by covering them with a protective coating of glass. This procedure effectively eliminated the numerous lines of the two metals and gave spectra of chlorine in which the hydrogen lines appeared as the only impurity.

TABLE 1.—*Wave lengths in the arc spectrum of chlorine*

λ I. A.	Intensity and notes	Wt.	ν	Term combinations	λ I. A.	Intensity and notes	Wt.	ν	Term combinations
9876.08	1	E	10122.70	$4s^3P_1-4p^3D_3$	8087.66	2	C	12361.12	$4x23-5p^3S_1$
9702.30	1	E	10304.01	$4s^1P_1-4p^1P_2$	8086.71	8	A	12362.57	
9592.25	2	C	10422.23	$4s^3P_2-4p^3D_3$	8085.57	6	A	12364.32	$4x22-5p^3S_1$
9584.80	0	E	10430.33	$4s^1P_2-4p^1P_2$	8084.51	4	A	12365.94	$4x21-5p^3S_1$
9486.88	0	E	10537.98	$4s^1P_1-4p^1P_1$	8051.03	2	B	12417.36	
9452.06	3	B	10576.80	$4s^3P_1-4p^3P_2$	8023.31	2	B	12460.26	
9393.85	1	E	10642.35	$4s^1P_2-4p^1P_2$	8017.54	1	E	12469.23	$4x23-5p^3P_2$
9288.84	4	A	10762.66	$4s^3P_2-4p^3D_3$	8015.58	4	B	12472.28	$4x22-5p^3P_1$
9197.47	1	D	10869.58	$4s^3P_1-4p^4S_2$	7997.84	6	A	12499.94	$4s^4P_2-4p^3D_2$
9191.71	5	B	10876.39	$4s^4P_2-4p^4P_1$	7980.61	1	E	12526.92	$4s^4P_2-4p^4D_1$
9121.12	8	A	10960.56	$4s^4P_2-4p^4P_2$	7976.97	3	B	12532.65	$4p^4P_1-3d^4D_2$
9073.17	6	B	11018.48	$4s^3P_1-4p^3S_1$	7974.74	2	C	12536.15	
9069.68	4	B	11022.72		7952.54	1	E	12571.15	
9045.43	7	B	11052.28	$4s^3P_1-4p^3P_1$	7935.01	2	C	12598.92	$4x21-5x25$
9038.98	5	B	11060.16		7933.88	4	B	12600.71	$4x22-5x25$
8948.01	10	A	11172.60	$4s^4P_2-4p^4P_2$	7924.67	8	A	12615.36	$4s^4P_1-4p^3P_2$
8912.90	8	A	11216.61	$4s^3P_2-4p^3P_2$	7915.10	3	B	12630.61	$4p^4P_1-3d^4D_1$
8846.07	0	E	11301.36	$4p^4D_3-3d^4D_3$	7899.36	5	B	12655.78	$4p^4P_2-3d^4D_2$
8711.45	0	E	11476.00	$4x22-5x26$	7878.24	8	A	12689.70	$4s^4P_2-4p^3D_2$
8686.30	8	A	11509.22	$4s^3P_2-4p^4S_2$	7840.66	0	E	12750.53	
8641.80	0	E	11568.49	$4p^4D_2-3d^4D_4$	7830.79	4	A	12766.60	$4p^4P_2-3d^4D_2$
8628.58	0	E	11586.21	$4x21-5p^3D_2$	7821.39	7	A	12781.94	$4p^4P_2-3d^4D_4$
8589.08	0	E	11639.50		7777.84	0	E	12853.51	
8585.99	15	A	11643.69	$4s^4P_2-4p^4D_3$	7771.13	1	E	12864.61	$4p^4P_2-3d^4D_1$
8577.95	1	E	11654.60	$4p^4D_3-3d^4D_2$	7769.18	4	A	12867.83	$4p^4P_1-3d^4D_2$
8575.27	12	A	11658.24	$4s^4P_1-4p^4D_2$ and $4s^3P_2-4p^3S_1$	7744.98	10	A	12908.04	$4s^4P_1-4p^4S_2$
					7717.60	9	A	12953.84	$4s^4P_2-4p^3P_2$
8550.50	4	C	11692.02	$4s^3P_2-4p^3P_1$	7702.87	1	E	12978.60	$4p^4P_2-3d^4D_2$
8497.30	0	E	11765.21	$4p^4D_3-3d^4D_2$	7692.94	0	E	12995.36	$4p^4D_2-6s^4P_2$
8467.32	4	C	11806.87	$4p^4D_4-3d^4D_4$	7672.46	5	B	13030.05	$4s^4P_2-4p^3D_2$
8428.27	15	A	11861.57	$4s^4P_1-4p^4D_1$					
					7659.47	0	E	13052.15	
8406.14	1	E	11892.83	$4p^4D_4-3d^4D_2$	7656.89	0	E	13056.54	$4s^4P_1-4p^3S_1$
8375.97	20	A	11935.64	$4s^4P_2-4p^4D_4$	7561.19	0	E	13221.80	
8333.31	15	A	11996.74	$4s^4P_2-4p^4D_2$	7547.09	12	A	13246.50	$4s^4P_2-4p^4S_2$
8304.65	0	E	12038.14	$4p^3P_2-6s^4P_2$	7492.10	3	B	13343.72	$4p^4D_4-6s^4P_2$
8286.54	0	E	12064.45		7489.46	2	B	13348.43	$4p^4D_3-6s^4P_2$
8280.82	0	E	12072.78	$4p^3D_3-5x25$	7462.40	2	B	13396.83	$4s^4P_2-4p^3S_1$ and $4p^4D_4-3d^4F_3$
8273.64	0	E	12083.26						
8268.98	0	E	12090.07		7459.46	1	E	13402.11	$4p^4D_3-3d^4F_4$
8267.39	0	E	12091.40	$4p^3P_2-3d^4F_3$	7454.23	0	E	13411.51	$4p^4D_1-6s^4P_1$
8258.30	0	E	12105.71		7444.35	1	E	13429.31	$4s^4P_2-4p^3P_1$
8221.76	12	A	12159.51	$4s^4P_2-4p^3D_3$	7435.68	2	B	13444.97	$4p^4D_4-3d^4F_4$
8220.45	8	A	12161.44	$4s^4P_1-4p^3D_2$	7414.12	12	A	13484.07	$4s^4P_2-4p^3P_2$
8212.03	10	A	12173.91	$4s^4P_2-4p^4D_3$	7382.50	1	E	13541.82	
8203.66	1	D	12186.34		7342.83	1	E	13615.00	$4p^4D_2-6s^4P_1$
8200.23	5	B	12191.43	$4x22-5p^3P_1$	7329.36	0	E	13640.00	$4p^4D_4-3d^4F_3$
8199.06	5	B	12193.17	$4x21-5p^3P_1$	7256.65	15	A	13776.67	$4s^4P_2-4p^4S_2$
8194.39	7	A	12200.12	$4s^4P_2-4p^4D_1$	7244.82	0	E	13799.16	
8170.02	0	E	12236.51	$4p^4D_2-5x25$	7195.04	1	E	13894.64	
8148.74	0	E	12268.46		7191.52	0	E	13901.44	
8094.75	0	E	12350.30		7094.29	1	D	14091.96	

TABLE 1.—*Wave lengths in the arc spectrum of chlorine*—Continued

λ I. A.	Intensity and notes	Wt.	ν	Term combinations	λ I. A.	Intensity and notes	Wt.	ν	Term combinations
7086.83	3	B	14106.80	$4p^4P_2-6s^4P_3$	5799.94	3	B	17236.79	
7008.18	1	E	14265.11		5796.34	3	A	17247.49	
6995.90	1	D	14290.15		5774.84	0 I?	E	17311.71	
6981.90	2	A	14318.81	$4p^4P_3-6s^4P_3$	5772.65	0	E	17318.27	
6966.95	1	D	14349.54	$4p^4P_2-6s^4P_2$	5731.77	0	E	17441.79	
6932.94	3	A	14419.92	$4p^4P_2-3d^4F_4$	5726.27	0	E	17458.54	
6854.50	0	D	14584.94		5702.05	0	E	17532.70	
6840.26	1	C	14615.30	$4p^4P_3-3d^4F_3$	5686.38	0	E	17581.01	
6810.08	1	C	14680.07		5580.52	0	D	17914.51	
6709.96	1	C	14899.11		5578.22	1	C	17921.90	$4p^4P_2-4d^4F_3$
6703.26	1	D	14914.01		5569.17	2	D	17951.03	
6678.45	1	C	14969.41	$4p^4P_2-6s^4P_1$	5549.32	0	E	18015.24	
6653.85	0	C	15024.75		5532.16	3	C	18071.11	$4p^4P_3-4d^4F_4$
6609.30	2	B	15126.03		5528.09	0	D	18084.42	
6604.61	2	B	15136.77	$4p^4D_3-4d^4D_3$	5514.71	2	C	18128.30	
6600.13	0	E	15147.02	$4x22-4d^4D_3$	5513.00	2	C	18133.92	$4p^4P_3-4d^4F_3$
6572.42	2	B	15280.65		5493.28	1 I?	D	18199.02	
6531.43	4	A	15306.36	$4p^4D_4-4d^4D_4$	5405.74	0	E	18493.75	
6502.28	1	C	15374.98	$4p^4D_4-4d^4D_3$	5404.01	0	E	18499.65	
6471.60	0	E	15447.87		5341.04	1	E	18717.75	
6453.34	0	E	15491.58		5330.79	0	E	18753.74	
6440.35	4	A	15498.74	$4p^2D_3-60$	5307.62	0	E	18835.61	
6434.80	5	A	15536.21		5140.38	1	C	19448.41	$4s^3P_1-5x24$
6425.64	2	B	15558.36		4976.65	4	B	20088.25	$4s^3P_2-5x24$
6408.08	1	C	15600.99		4852.72	4	B	20601.26	$4s^3P_2-5p^4D_3$
6398.64	7	A	15624.01		4818.55	2	C	20747.35	$4s^3P_1-5p^4S_2$
6394.77	0	D	15633.47		4740.68	5	B	21088.14	$4s^3P_2-5p^4D_2$
6371.48	0 Si?	D	15690.62		4721.28	3	B	21174.79	$4s^3P_2-5p^2D_2$
6347.05	1	D	15751.00		4691.54	4	A	21309.02	$4s^3P_2-5p^4D_1$
6341.70	3	B	15764.29		4677.76	2	A	21371.79	$4s^3P_2-5x26$
6335.08	0	E	15780.77		4661.22	8	A	21447.62	$4s^3P_1-5p^2P_1$
6321.65	1	B	15814.29		4654.06	4	A	21480.62	$4s^3P_2-5p^2D_2$
6306.77	0	E	15851.60		4623.96	3	A	21620.45	$4s^3P_1-5p^2S_1$
6291.86	0	E	15889.17		4601.00	10	A	21728.34	$4s^3P_1-5p^2P_2$
6280.29	1	D	15918.44		4578.18	1	B	21836.64	$4s^4P_1-5p^4P_2$
6252.34	2	C	15989.60	$4p^4P_1-4d^4D_2$	4526.21	12	A	22087.37	$4s^2P_2-5p^2P_1$
6242.66	1	C	16014.39	$4p^4D_3-60$	4491.08	4	A	22260.14	$4s^2P_2-5p^2S_1$
6231.57	2	B	16042.89	$4p^4P_1-4d^4D_1$	4475.31	6	A	22338.57	$4s^4P_2-5p^4D_3$
6226.48	0	D	16056.00		4469.37	6	A	22368.26	$4s^2P_2-5p^2P_2$
6211.61	2	B	16094.44	$4p^4D_4-59$	4446.12	2	B	22485.23	$4s^4P_2-5p^4P_1$
6194.75	4	B	16138.24	$4p^4P_2-4d^4D_3$	4445.82	2	B	22486.75	$4s^4P_1-5p^4D_2$
6162.14	3	C	16223.65	$4p^4P_3-4d^4D_2$	4438.48	7	A	22523.93	$4s^4P_1-5p^4P_2$
6141.87	0	E	16277.19	$4p^4P_2-4d^4D_1$	4403.03	6	A	22705.28	$4s^4P_2-5p^4P_2$
6140.25	6	A	16281.49	$4p^4P_3-4d^4D_4$	4402.52	1	E	22707.91	$4s^4P_1-5p^4D_1$
6114.41	4	A	16350.29	$4p^4P_3-4d^4D_3$	4390.38	4	A	22770.70	$4s^4P_1-5x26$
6082.63	0 I?	C	16435.72	$4p^4P_3-4d^4D_2$	4389.76	12	A	22773.91	$4s^4P_3-5p^4D_4$
6028.38	0	E	16583.62		4387.53	3	A	22785.49	$4s^4P_1-5p^4S_2$
6019.80	1	D	16607.26		4379.91	7	A	22825.13	$4s^4P_3-5p^4D_3$
5991.46	0	E	16685.81		4371.55	1	B	22868.78	$4s^4P_3-5p^4D_3$
5987.78	0	E	16696.07		4369.52	6	A	22879.40	$4s^4P_1-5p^2D_2$
5965.74	0	E	16757.75		4363.30	6	A	22912.02	$4s^4P_2-5p^2D_2$
5930.42	1	D	16857.55	$\{4p^4D_3-4d^4F_4$ / $4p^4P_2-59$	4323.34	6	A	23123.79	$4s^4P_3-5p^4S_2$
					4264.58	3	A	23442.39	$4s^4P_2-5p^2D_2$
5922.31	0	E	16880.64		4226.43	5	A	23653.99	$4s^4P_2-5p^4S_2$
5913.82	0	E	16904.87						
5908.25	0	E	16920.81	$4p^4D_3-4d^4F_3$	4209.67	4	A	23748.17	$4s^4P_3-5p^2D_2$
					4208.00	2	B	23757.59	
5866.73	0	E	17040.56		4185.52	1	B	23885.19	
5856.74	2	B	17069.62	$4p^4P_3-59$	4032.19	2	A	24793.44	
5847.74	2	C	17095.90	$4p^4D_4-4d^4F_4$					
5846.71	2	C	17098.91						
5844.27	1	D	17106.04						
5842.40	0	E	17111.52						
5839.89	0	D	17118.88						
5806.86	0	E	17216.25						
5802.91	1	C	17227.97	$4p^4P_2-60$					
5801.36	0	E	17232.57						

IV. STRUCTURE OF THE ARC SPECTRUM

According to the spectroscopic alternation law, the arc spectrum of chlorine should consist of multiplets representing combinations of terms of even multiplicity. These terms, in accordance with Hund's theory, arise from the various configurations assumed by the seven valence electrons which lie outside the closed shells of the preceding rare gas, neon. In the unexcited state of the Cl atom two of these electrons occupy 3_1 orbits, and five are assigned to 3_2 orbits, which is expressed by the symbol s^2p^5. The term which is therefore characteristic of the normal state is an inverted ^2P; that is, the component with inner quantum number $j=3/2$ lies lowest. Throughout this paper the use of cumbersome fractional inner quantum numbers is avoided by assigning to each term an integral inner quantum number one-half unit greater than the true value.

The terms which represent the excited states of the atom result from the interaction of the series electron with the electron group s^2p^4 which characterizes the unexcited state of the ion Cl^+. The terms arising from the configuration s^2p^4 are ^1S, ^1D, and ^3P, of which the latter is lowest and has already been established for Cl II by Bowen.[18] We may therefore obtain the terms representing the excited states of the neutral atom by finding the resultants gotten by adding in turn the electrons *ns*, *np*, *nd*, etc., to the terms ^1S, ^1D, and ^3P. In Table 2 are given the theoretical terms which may be expected to account for the lines presented in Table 1.

TABLE 2.—*Theoretical terms of Cl I*

Electron configuration	Basic term of Cl II		
	^3P	^1D	^1S
$3s^2 \cdot 3p^5$	**^3P**		
$3s^2 \cdot 3p^4 \cdot 3d$	^3P, ^3D, ^3F, ^1P, **^1D, ^1F**	^3S, ^3P, ^3D, ^3F, ^3G	^3D
$3s^2 \cdot 3p^4 \cdot 4s$	**^3P, ^1P**	^3D	^3S
$3s^2 \cdot 3p^4 \cdot 4p$	**^3S, ^3P, ^3D, ^1S, ^1P, ^1D**	^3P, ^3D, ^3F	^3P
$3s^2 \cdot 3p^4 \cdot 4d$	^3P, ^3D, ^3F, ^1P, **^1D, ^1F**	^3S, ^3P, ^3D, ^3F, ^3G	^3D
$3s^2 \cdot 3p^4 \cdot 5s$	^3P, **^1P**	^3D	^3S
$3s^2 \cdot 3p^4 \cdot 5p$	**^3S, ^3P, ^3D, ^1P, ^1P, ^1D**	^3P, ^3D, ^3F	^3P
$3s^2 \cdot 3p^4 \cdot 6s$	^3P, **^1P**	^3D	^3S

The terms which have actually been found for Cl I are given in Table 3. It has been possible to identify most of these terms with the theoretical ones of Table 2, and wherever this has been done the fact is indicated in Table 2 by printing the symbol in heavy type. Complex terms of Cl I which are based on ^3P of the ion may be expected to have widely separated components, whereas terms derived from ^1S and ^1D will exhibit only narrow separations. An inspection of Table 3 shows that most of the terms listed therein are based on

[18] Phys. Rev., **31**, p. 34; 1928.

^3P, the others apparently originating either with ^1S or ^1D. The uncertainty of establishing the origin of these terms, giving groups of lines with fine structure, is discussed below. No comment is needed to interpret Table 3 other than to state that the numerical values of the terms are absolute; that is, they are based on what is believed to be the most probable value of the ground term $^2P_2$. The derivation of this value from the series limits is described in a subsequent paragraph. Figure 4 illustrates graphically the data of Table 3.

TABLE 3.—*Terms of Cl I*

Term No.	Term type	ν	$\Delta\nu$	Series electron	Term No.	Term type	ν	$\Delta\nu$	Series electron
1	$^3P_2$	104991.			31	$^4D_3$	10168.25		
			881.	$3p$				486.68	
2	$^3P_1$	104110.			32	$^4D_2$	9681.57		
								221.08	
3	$^4P_3$	33037.00			33	$^4D_1$	9460.49		
			530.20						
4	$^4P_2$	32506.80			34	$^4S_2$	9382.70		
			338.44						
5	$^4P_1$	32168.36		$4s$	35	$^2D_3$	9594.69		$5p$
								305.70	
6	$^2P_2$	30769.56			36	$^2D_2$	9288.99		
			639.80						
7	$^2P_1$	30129.76			37	$^2P_2$	8682.16		
								280.80	
8	$^4P_3$	22076.46			38	$^2P_1$	8401.36		
			212.05						
9	$^4P_2$	21864.41			39	$^2S_1$	8509.37		
			233.96						
10	$^4P_1$	21630.45			40	$^4D_4$	9294.51		
								85.92	
11	$^4D_4$	21101.36			41	$^4D_3$	9208.59		
			238.26					110.75	
12	$^4D_3$	20863.10			42	$^4D_2$	9097.84		
			353.01					98.02	
13	$^4D_2$	20510.09			43	$^4D_1$	8999.82		
			203.36						$3d$
14	$^4D_1$	20306.73		$4p$	44	$^4F_5$	?		
15	$^2D_2$	20347.31			45	$^4F_4$	7656.40		
			340.35					195.25	
16	$^2D_3$	20006.96			46	$^4F_3$	7461.15		
17	$^2P_2$	19552.96			47	$^4F_2$	?		
			475.40						
18	$^2P_1$	19077.56			48	$^4P_3$	7757.63		
								242.83	
19	$^2S_2$	19260.32			49	$^4P_2$	7514.80		$6s$
								619.76	
20	$^2S_1$	19111.28			50	$^4P_1$	6895.04		
21	^2X	20875.32			51	$^4D_4$	5794.98		
			1.70					68.69	
22	^2X	20873.62		$4x$	52	$^4D_3$	5726.29		
			3.08					85.51	
23	^2X	20870.54			53	$^4D_2$	5640.78		
								53.39	
24		10681.33			54	$^4D_1$	5587.39		$4d$
25		8274.65		$5x$	55	$^4F_5$	?		
26		9397.72			56	$^4F_4$	4005.40		
								62.87	
27	$^4P_3$	10513.07			57	$^4F_3$	3942.53		
			181.35						
28	$^4P_2$	10331.72			58	$^4F_2$	?		
			310.15	$5p$					
29	$^4P_1$	10021.57			59	?	5006.88		
30	$^4D_4$	10263.09			60	?	4848.59		
			94.84						

Since no Zeeman effects are available to reveal the identity of the chlorine arc lines, the classification of the lines into multiplets had to be based mainly on the evidence furnished by recurring constant wave-number differences, line intensities, and analogies with other spectra whose structures are theoretically the same as that of Cl I. The important $\Delta\nu$'s to be sought for were revealed to some extent by Turner's lines and by the earlier investigations of de Bruin,[19] who found the separation $\Delta\nu = 530.2$ occurring conspicuously among the lines ascribed to the arc by Nelthorpe. The constant differences discovered by Paulson,[20] which are real, appear to be characteristic of spark lines only.

In Tables 4 to 9 are presented the principal multiplets which contain most of the prominent lines of Cl I. In many of the multiplets the full complement of lines has not been observed. These fainter lines, whose wave lengths may be calculated from the term combinations, are indicated in the tables by braces $\left\{\quad\right\}$. The resonance lines lie in the Schumann region and were first observed by Turner. The interpretation of these lines as resulting from the electron transition $4s \rightarrow 3p$ has already been announced by Bowen [21] and by Laporte.[22] The prominent multiplets lying in the near infra-red, shown in Table 5, represent the transition of the series electron from the $4p$ state to the $4s$ state. It is to be noted that among these the intersystem combination $^2P_2 - {}^4P_{123}$ is very strong. It is to be noted further that the separations of the $4p$ terms (^4D, ^4P) deviate strongly from the Landé interval rule. This indicates an anomalous coupling which becomes much more developed with the $5p$ terms and makes it difficult to identify those of the quartet system. The combinations which have been found lie in the blue and violet and are set forth in Table 6.

[19] K. Akad. Wet. Amsterdam, **30**, p. 20; 1926. Zeit. für Physik, **39**, p. 869; 1926.
[20] Astrophys. J., **40**, p. 298; 1914.
[21] Phys. Rev., **31**, p. 498; 1928.
[22] Nature, **121**, p. 1021; 1928.

It seems probable that the infra-red lines with fine structure, Table 7, represent combinations between the $5p$ doublet terms and terms arising from ^1D or ^1S of the ion. A satisfactory identification

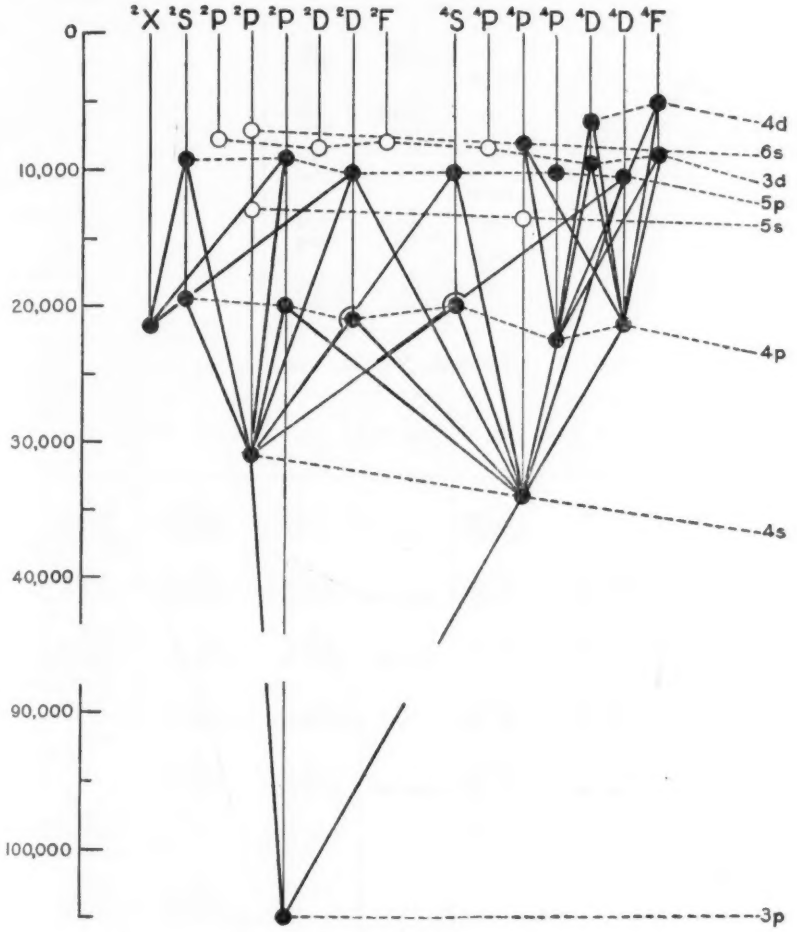

FIGURE 4.—*Term diagram of Cl I*

of these terms, numbered 21, 22, and 23, in Table 10, has not yet been found. They are shown in Figure 4 on the line labeled ^2X and should consist of at least two term groups if the parent term of the ion is ^1S or ^1D.

TABLE 4.—*Turner's lines*

4s \ 3p	$^3P_1$ 881 $^3P_2$
$^3P_2$	5 1363.5 73342 — 5 1347.2 74225
639.80	
$^3P_1$	3 1351.7 73979 — 2 1335.8 74863
$^1P_1$	— { 1389.8 71954 }
530.20	
$^1P_2$	3 1396.5 71607 — 5 1379.6 72484
338.44	
$^1P_1$	4 1389.9 71946 — { 1373.2 72825 }

TABLE 5.—*Multiplets from the transition 4p→4s*

4s \ 4p	$^3P_1$ 639.80 $^3P_2$	1398.80	$^1P_1$ 338.40 $^1P_2$ 530.20 $^1P_3$
$^3D_3$	2 9592.25 10422.23		12 8221.76 12159.51 — 8 7878.24 12689.70
340.35			
$^3D_2$	1 9876.08 10122.70 — 4 9288.84 10762.66	1398.78	8 8220.45 12161.44 — 6 7997.84 12499.94 — 5 7672.46 13030.05
$^3P_2$	3 9452.06 10576.80 — 8 8912.90 11216.61	1398.75	8 7924.67 12615.36 — 9 7717.60 12953.84 — 12 7414.12 13484.07
475.40			
$^3P_1$	7 9045.43 11052.28 — 4 8550.50 11692.02		{ 7636.8 13090.8 } — 1 7444.35 13429.31
$^3S_1$	6 9073.17 11018.48 — 12 8575.27 11658.24	1398.30	0 7656.89 13056.54 — 2 7462.40 13396.83
$^1D_4$			20 8375.97 11935.64
238.26			
$^1D_3$			15 8585.99 11643.69 — 10 8212.03 12173.91
353.01			
$^1D_2$			12 8575.27 11658.24 — 15 8333.31 11996.74 — 1 7980.61 12526.92
203.36			
$^1D_1$			15 8428.27 11861.57 — 7 8194.39 12200.12
$^1P_3$			0 9584.80 10430.33 — 8 9121.12 10960.56
212.05			
$^1P_2$			1 9702.30 10304.01 — 1 9393.85 10642.35 — 10 8948.01 11172.60
233.96			
$^1P_1$			0 9486.88 10537.98 — 5 9191.71 10876.39
$^1S_1$	1 9197.47 10869.58 — 8 8686.30 11509.22	1398.82	10 7744.98 12908.04 — 12 7547.09 13246.50 — 15 7256.65 13776.67

TABLE 6.—*Multiplets from the transition 5p→4s*

4s / 5p	$^3P_1$	639.80	$^3P_2$	1398.80	$^1P_1$	338.40	$^1P_2$	530.20	$^1P_3$
$^3D_3$			3 4721.28 21174.79				6 4363.30 22912.02		3 4264.58 23442.39
305.70									
$^3D_2$	{4796.9} {20840.8}		4 4654.06 21480.62	1398.78	6 4369.52 22879.40		1 4305.87 23217.60		4 4209.67 23748.17
$^3P_2$	8 4661.22 21447.62		12 4526.21 22087.37						
280.80									
$^3P_1$	10 4601.00 21728.34		6 4469.37 22368.26						
$^3S_1$	3 4623.96 21620.45		4 4491.08 22260.14						
$^1D_4$									12 4389.76 22773.91
94.84									
$^1D_3$			4 4852.72 20601.26				6 4475.31 22338.57		1 4371.55 22868.78
486.68									
$^1D_2$	{4889.1} {20448.1}		5 4740.68 21088.14	1398.61	2 4445.82 22486.75		7 4379.91 22825.13		{4280.5} {23355.3}
221.08									
$^1D_1$	{4836.7} {20669.2}		4 4691.54 21309.02	1398.89	1 4402.52 22707.91		{4337.9} {23046.3}		
$^1P_3$							{4545.5} {21993.7}		7 4438.48 22523.93
181.35									
$^1P_2$					1 4578.18 21836.64		{4508.3} {22175.0}		6 4403.03 22705.28
310.15									
$^1P_1$					{4514.1} {22146.8}		2 4446.12 22485.23		
$^1S_2$	2 4818.55 20747.35		{4674.4} {21386.8}		3 4387.53 22785.49		6 4323.34 23123.79		5 4226.43 23653.99

TABLE 7.—*Combinations of doublet terms with fine-structure terms*

5p / 4x	$^2S_1$	$^2P_1$	$^2P_2$	$^2D_2$	$^2D_3$
21	4 8084.51 12365.94	5 8199.06 12193.17		0 8628.58 11586.21	
1.70					
22	6 8085.57 12364.32	5 8200.23 12191.43	4 8015.58 12472.28		
3.08					
23	2 8087.66 12361.12		1 8017.54 12469.23		

TABLE 8.—*Multiplets from the transition 3d→4p*

3d \ 4p	$^4P_1$	233.96	$^4P_2$	212.05	$^4P_3$	$^4D_1$	203.36	$^4D_2$	353.01	$^4D_3$	238.26	$^4D_4$
$^4D_4$					7 7821.39 12781.94					0 8641.80 11568.49		4 8467.32 11806.87
85.92												
$^4D_3$			5 7899.36 12655.78		4 7769.18 12867.83			0 8846.07 11301.36		1 8577.95 11654.60		1 8406.14 11892.83
110.75												
$^4D_2$	3 7976.97 12532.65		4 7830.79 12766.60		1 7702.87 12978.60	(8919.2) (11208.7)		(8760.2) (11412.1)		0 8497.30 11765.21		
98.02												
$^4D_1$	3 7915.10 12630.61		1 7771.13 12864.61			(8841.9) (11306.7)		(8685.6) (11510.1)				
$^4F_5$												2 7462.40 13396.83
?												
$^4F_4$					3 6932.94 14419.92							2 7435.68 13444.97
195.25										(7569.8) (13206.7)		
$^4F_3$			(6940.9) (14403.3)		1 6840.26 14615.30			(7661.3) (13049.1)		1 7459.46 13402.11		0 7329.36 13640.00
?												
$^4F_2$	(6818.4) (14662.1)		(6711.4) (14896.0)		(6617.1) (15108.1)	(7495.1) (13338.4)		1 7382.50 13541.82		1 7195.04 13894.64		

TABLE 9.—*Multiplets from the transitions 4d→4p and 6s→4p*

4d \ 4p	$^4P_1$	233.96	$^4P_2$	212.05	$^4P_3$	$^4D_1$	203.36	$^4D_2$	353.01	$^4D_3$	238.26	$^4D_4$
$^4D_4$					6 6140.25 16281.49					(6634.7) (15068.1)		4 6531.43 15306.36
68.69												
$^4D_3$			4 6194.75 16138.24		4 6114.41 16350.29			(6762.3) (14783.8)		2 6604.61 15136.77		1 6502.28 15374.98
85.51												
$^4D_2$	2 6252.34 15989.60		3 6162.14 16223.65		0 6082.63 16435.72	(6816.7) (14665.8)		(6723.5) (14869.2)		(6567.6) (15222.2)		
53.39												
$^4D_1$	2 6231.57 16042.89		0 6141.87 16277.19			(6792.0) (14719.2)		(6699.4) (14922.6)				
$^4F_5$												?
?												
$^4F_4$					3 5532.16 18071.11					1 5930.42 16857.55		2 5847.74 17095.90
62.93												
$^4F_3$			1 5578.22 17921.90		2 5513.00 18133.92			(6034.1) (16567.8)		0 5908.25 16920.81		(5826.2) (17159.1)
?												
$^4F_2$	?		?		?	?		?		?		

6s \ 4p												
$^4P_3$			3 7086.83 14106.80		2 6981.90 14318.81			(7839.5) (12752.4)		(7628.3) (13105.4)		3 7492.10 13343.72
242.83												
$^4P_2$	(7082.0) (14115.5)		1 6966.95 14349.54		0 6865.50 14561.57	(7815.2) (12792.0)		0 7692.94 12995.36		2 7489.46 13348.43		
619.76												
$^4P_1$	(6784.5) (14735.4)		1 6678.45 14969.41			0 7454.23 13411.51		1 7342.83 13615.00				

TABLE 10.—*Series limits of Cl I*

Term sequence	Limiting term of Cl^+			$^3P_2-{}^3P_3$
	$^3P_0$	$^3P_1$	$^3P_2$	
$4p, 5p, {}^2P_3$	106491			105493
$4p, 5p, {}^2P_1$		106661		105963
$4s, 6s, {}^4P_3$			104723	104723
$4s, 6s, {}^4P_2$			104920	104920
$4s, 6s, {}^4P_1$		105573		104875
$4p, 5p, {}^4P_3$			105001	105001
$4p, 5p, {}^4P_2$			105167	105167
$4p, 5p, {}^4P_1$		105516		104818
$4p, 5p, {}^4D_4$			104890	104890
$4p, 5p, {}^4D_3$			104911	104911
$4p, 5p, {}^4D_2$			105467	105467
$4p, 5p, {}^4D_1$			105697	105697
$4p, 5p, {}^2D_3$		105524		104826
$4p, 5p, {}^2D_2$		105602		104904
$4p, 5p, {}^4S_2$		105269		104571
$4p, 5p, {}^2S_1$	106082			105084
$3d, 4d, {}^4D_4$			104578	104578
$3d, 4d, {}^4D_3$			104635	104635
$3d, 4d, {}^4D_2$			104695	104695
$3d, 4d, {}^4D_1$			104709	104709
$3d, 4d, {}^4F_4$			104964	104964
$3d, 4d, {}^4F_3$			104914	104914
Means	106286	105691	104948	104991

$^3P_0-{}^3P_1 : {}^3P_1-{}^3P_2$ { calculated 595 : 743 / observed 300 : 698

Ionization potential $= 1.2345 \times 104991 \times 10^{-4} = 12.96v$

The ^4P and ^4D terms coming from the $4p$ electron combine with higher ^4P, ^4D, and ^4F terms, coming from the $3d$, $6s$, and $4d$ electrons, to give the multiplets of Tables 8 and 9. The identity of the $4d$ electron is not absolutely certain. The ^4D and ^4F terms could, as well, come from a $4f$ electron. But we are inclined to the belief that it is $4d$ for the following reasons: (1) There is a close parallelism between the intensities of the lines in the multiplets arising from it and the corresponding ones coming from the $3d$ electron; (2) the term separations are all smaller than in $3d$ ^4D, which is a necessary characteristic (discussed below) of nd ^4D terms in Rydberg sequence and approaching a common limit in the ion; (3) the values for the series limits from these terms, on the assumption that they are in sequence, are in excellent accord with those given by the other series.

The terms coming from the $5s$ electron have not been found. Of these, the more prominent would be ^2P and ^4P, with values lying between 13,000 and 15,000. Their combinations, therefore, with the terms arising from the $4p$ and $5p$ electrons would fall in the infra-red beyond the domain accessible to the sensitized photographic plate.

In Figure 4 series-forming terms are plotted on the same vertical line. An inspection of the figure shows at least seven sets of terms which are available for calculating series limits, and nine if the terms ^4D and ^4F are correctly attributed to the $4d$ electron. In only one sequence are more than two terms known. For this reason

it did not seem justifiable to seek more accurate values for the terms than those to be found by substitution in Rydberg's formula.

The solution is readily effected by the use of a suitable table such as Table 3 of Fowler's Report. By adding to the term values thus obtained the amounts of their relative separations from the basic term $^2P_2$ we obtain the distances between the limiting terms of the ion and the lowest term of the neutral atom. The limits to which the component series converge are the components of the ground term $^3P_{0,1,2}$ of the ion. This term, established for Cl II by Bowen, is characterized by the separations $\Delta\nu_{0,1}=300$, $\Delta\nu_{1,2}=698$, the component $^3P_2$ being lowest. In Table 10 the values found from all the component series are presented. It is seen that only two values are available for fixing the position of $^3P_0$. Of these, the first appears to be erratic and when averaged with the other gives a value for the difference $^3P_0-{}^3P_1$ nearly twice that found by observation. The value of the difference $^3P_1-{}^3P_2$, however, from the calculated series limits is in excellent agreement with that observed. The observed separations $^3P_1-{}^3P_2=698$ and $^3P_0-{}^3P_2=998$ have been applied to the individual determinations of the limits $^3P_1$ and $^3P_0$ to give the value of the limit $^3P_2$. The mean value found for the separation of the lowest levels of the neutral atom and the ion is $^2P_2-{}^3P_2=104991$ cm^{-1}, and from this an ionization potential of 12.96 volts is derived. This value differs only slightly from the value 13.0 volts found by linear interpolation between the ionization potentials of 10.31 volts for S I. (Hopfield) [23] and 15.69 volts for A I. (Meissner).[24]

Based on theoretical considerations, Hund [25] has given a schematic representation of the structure of a halogen spectrum and has indicated the manner in which the various series approach their limits. That his procedure did not lead to correct results for spectra built up on inverted terms has already been pointed out by Shenstone [26] for Ne, Ni, Pd, and other spectra. With the detection of the higher series terms of Cl I we saw that for this spectrum also Hund's procedure would not give correct results. For instance, the term separations (530.20; 338.40) of $4s\ ^4P_{3,2,1}$ and (242.83; 629.76) of $6s\ ^4P_{3,2,1}$ indicate that in approaching the limit the separation $\Delta\nu_{3,2}$ decreases while $\Delta\nu_{2,1}$ increases. If Hund's scheme were correct, we should expect $\Delta\nu_{3,2}$ to increase and $\Delta\nu_{2,1}$ to decrease. It may be noted here, in this connection, that we have found in Br I this anomalous coupling appears in the term $5s\ ^4P_{3,2,1}$, which is analogous to $4s\ ^4P_{3,2,1}$ of Cl I, the separation $\Delta\nu_{3,2}$ being smaller than $\Delta\nu_{2,1}$. It is thus clear that in the series of ^4P terms coming from the *ns* electrons the components $^4P_{3,2}$ approach $^3P_2$ of the ion as limit, and $^4P_1$ approaches $^3P_1$ as limit.

[23] Nature, **112**, p. 437; 1923.
[24] Zeit. für Physik, **40**, p. 844; 1927.
[25] Linienspektren und periodisches System der Elemente, p. 198; 1927. Julius Springer, Berlin.
[26] Phys. Rev., **30**, p. 380; 1927. Nature, **121**, p. 619; 1928; **122**, p. 727; 1928.

Again, in the series of ^4P terms coming from the *np* electrons we observe that the separations $\Delta\nu_{3,2}$ are smaller than $\Delta\nu_{2,1}$, which we interpret as indicating that the components $^4P_{3,2}$ approach $^3P_2$ of Cl II as limit, and $^4P_1$ approaches $^3P_1$ as limit.

We find that the identification of series limits just presented is in strict harmony with the new theoretical considerations of Hund [27] which have just come to our notice. For series terms coming from the *s* and *p* electrons his revised scheme is as follows:

$p^2P_2,\ p^2S_1,\ s^2P_1$ ---------- $\rightarrow\ ^3P_0$

$p^4P_1,\ p^4S_2,\ p^2D_{3,2},\ p^2P_1,\ s^4P_1,\ s^2P_2$ ---------- $\rightarrow\ ^3P_1$

$p^4D_{4,3,2,1},\ p^4P_{3,2},\ s^4P_{3,2}$ ---------- $\rightarrow\ ^3P_2$

To show the manner in which series terms coming from *nd* electrons approach their limits, we have extended Hund's scheme as follows:

$^2P_{2,1}$ ---------- $\rightarrow\ ^3P_0$

$^4P_{2,1},\ ^2D_{3,2},\ ^2F_{4,3}$ ---------- $\rightarrow\ ^3P_1$

$^4P_3,\ ^4D_{4,3,2,1},\ ^4F_{5,4,3,2}$ ---------- $\rightarrow\ ^3P_2$

It is thus seen that all the components of ^4D series approach a common limit, which means that the term separations of the higher series members become progressively smaller. It is this fact that has induced us to regard the ^4D and ^4F terms, discussed above, as belonging to the *nd* sequence.

No Zeeman effects for chlorine arc lines have ever been observed. The few observations published by Kimura and Fukuda [28], refer only to spark lines. In view of this situation we have relied on the analogies afforded by the first spark spectrum of argon, of which the structure has been worked out by deBruin [29], and confirmed by Zeeman effects, to work out the classification of Cl I described above. And the conclusions thus arrived at have been further strengthened on the detection by deBruin [30], of similar structures in the spectrum K III.

Theoretically the structures of Cl I and A II should be similar. The extent to which the actual classification of the spectra bears out the similarity may be seen by comparing the term diagram of Cl I (fig. 4) with that of A II given by deBruin in the work referred to. The following table gives a comparison of the corresponding term separations.

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[27] Zeit. für Physik, **52**, p. 601; 1928.

[28] Mem. College Sci. Kyoto Imperial Univ., **4**, p. 159; 1920.

[29] K. Akad. Wet. Amsterdam, **37**, p. 553; 1928. Zeit. für Physik, **48**, p. 62; 1928. Zeit. für Physik, **51**, p. 101; 1928.

[30] Science, **69**, p. 47; 1929. K. Akad. Wet. Amsterdam, **37**, p. 984; 1928. Zeit. für Physik, **53**, p. 658; 1929.

TABLE 11.—*Comparison of Cl I with A II and K III*

Term	Cl I	A II	K III
$3p\ {}^2P_{2,1}$	881	1,431	2,164
$4s\ {}^4P_{3,2}$	530.20	844.40	1,265.9
$4s\ {}^4P_{2,1}$	338.44	515.70	773.5
$4s\ {}^2P_{2,1}$	639.80	1,014.74	1,506.9
$4p\ {}^4P_{3,2}$	212.05	307.75	400.2
$4p\ {}^4P_{2,1}$	233.96	357.30	542.9
$4p\ {}^4D_{4,3}$	238.26	439.36	613.6
$4p\ {}^4D_{3,2}$	353.01	494.57	721.8
$4p\ {}^4D_{2,1}$	203.36	260.32	361.4
$4p\ {}^2D_{3,2}$	340.35	663.90	995.3
$4p\ {}^2P_{2,1}$	475.40	−532.96	
$3d\ {}^4D_{4,3}$	85.92	153.98	
$3d\ {}^4D_{3,2}$	110.75	149.62	
$3d\ {}^4D_{2,1}$	98.02	107.03	

The term $5p\ {}^2P_{2,1}$ of Cl I has not been found in A II. In both spectra it is to be seen that the term separations $4p\ {}^4P_{3,2}$ are smaller than $4p\ {}^4P_{2,1}$. It was these facts which led to the coordination of the term sequences with series limits discussed above. These anomalies are already apparent in the corresponding spectra of F I and Ne II, where the separations in the analogous terms $3p\ {}^4P_{3,2,1}$ show marked deviations from Landé's interval rule, although ${}^4P_{2,1}$ is actually smaller than ${}^4P_{3,2}$.

In both Cl I and A II the terms $4s\ {}^4P_{3,2,1}$ exhibit normal coupling; that is, the separations ${}^4P_{3,2}$ are larger than ${}^4P_{2,1}$ and approximately in the ratio required by the interval rule. In A II, however, the term $5s\ {}^4P_{3,2,1}$ shows abnormal coupling, $\Delta\nu_{3,2}=627.76$, and $\Delta\nu_{2,1}=729.14$. Although the corresponding term of Cl I has not been located, the $5s\rightarrow 4p$ combinations coming far in the infra-red, yet we may with confidence expect it to show the same anomaly as in A II, since in the following member of the sequence, $6s\ {}^4P_{3,2,1}$, the effect is quite pronounced. Here $\Delta\nu_{3,2}=242.83$ and $\Delta\nu_{2,1}=619.76$, the total separation being nearly the same as that of $4s\ {}^4P$.

Comparison of the term diagrams of Cl I and A II illustrates further the increasing stability, with increasing nuclear charge, of electron configurations containing d electrons. For Cl I the terms above the ground state in the order of stability are those from the $4s$, $4p$ ($5s$), $5p$, $3d$, etc., electrons. The multiplets coming from the $3d$ terms are relatively weak and incomplete. For A II, however, the $3d$ terms appear immediately after the $4s$ terms and give rise to prominent multiplets. Cl I and A II thus illustrate the atomic property which led Bohr [31] to predict a ${}^2D$ term as lowest in Sc III from the increasing stability of the 3_3 orbits revealed by a comparison of Ca II with K I. More recently Laporte [32] has pointed out a similar prop-

[31] Zeit. für Physik. **9**, p. 46; 1922.
[32] J. Opt. Soc. Am., **13**, p. 1; 1926.

erty of the heavier atoms of the second long period, and Laporte and Lang [33] have shown that it exists for the isoelectronic systems of Ni, Cu^+, and Zn^{++}.

V. CONCLUSION AND ACKNOWLEDGMENTS

A count of the lines of Table 1 shows that 62 per cent of them have been classified on the basis of the terms of Table 3. Of those remaining unclassified, only a few may be designated as strong lines. Three of these lie in the infra-red and two in the orange. All the other unclassified lines are faint and show on the spectrograms only after long exposures. The group of faint lines between 8260 and 8300 A is only incompletely measured. The original spectrogram shows a group of very close lines (fine-structure groups?) of which it was possible to see only the stronger ones under the measuring microscope. Not all of the faint lines in the table may be emitted by the Cl atom, but, in view of the fact that many of them represent permissible term combinations, all that have been measured are retained in the present list to await the test of future observations. These faint lines, if real, may owe their origin to the terms coming from ^1S and ^1D of the ion, but not yet established.

The question as to the existence of chlorine in the sun's reversing layer may now be answered. It was natural for astrophysicists to look toward the lighter halogens as a possible origin for the numerous unidentified Fraunhofer lines. But, as we have seen from the foregoing analysis of the Cl spectrum, the only lines that might be likely to occur are those from the $4p \rightarrow 4s$ transition, and these all lie in the near infra-red. Comparing the wave lengths of Table 1 with those of the sun presented in the recent Mount Wilson Revision of Rowland's Preliminary Table of Solar Spectrum Wave Lengths,[34] it is seen that only a few of the relatively faint chlorine lines are in approximate agreement with solar lines. These lines are not of the class of ultimate or penultimate lines, as defined by Russell,[35] and we must, therefore, conclude that there is no evidence at present for the existence of chlorine in the sun.

In addition to extending our knowledge of the arc spectrum of chlorine the experiments on which this paper is based have also yielded wave-length data for the spark spectra emitted by the singly and doubly ionized ions. We have made some progress in the classification of these lines and expect to give a report of this work, in the near future, in this journal.

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[33] Phys. Rev., **30**, p. 378; 1927.
[34] Carnegie Institution of Washington Publication No. 396; 1928.
[35] Astrophys. Jl., **61**, p. 223; 1925.

In conclusion, we wish to express our indebtedness to Dr. E. Wichers and Dr. B. H. Carroll, of the bureau staff, who at various times prepared the auric chloride used in this investigation. To Bourdon F. Scribner, also of the bureau staff, we are indebted for valued assistance in the computation of the wave lengths here presented. One of us (T. L. deB) desires to thank the International Education Board for the grant of a fellowship at the Bureau of Standards, which has made possible his cooperation in this investigation.

WASHINGTON, February 20, 1929.

POTENTIAL DIFFERENCES ACROSS THE BOUNDARIES BETWEEN SOLUTIONS OF MIXED UNIVALENT CHLORIDES

By Edgar Reynolds Smith

ABSTRACT

Potential differences across the boundaries between solutions of mixed univalent chlorides were measured using a flowing junction and silver-silver chloride electrodes. There is no evidence of complex formation, and the constant ion conductance principle which MacInnes has shown to be valid in solutions of pure univalent chlorides is probably equally valid in their mixtures.

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I. INTRODUCTION

In this investigation liquid junction potentials of the types

$$\begin{matrix} \text{NaCl } (0.1\,x_1) \\ \text{HCl } (0.1-0.1\,x_1) \end{matrix} \Big| \begin{matrix} \text{HCl } (0.1-0.1\,x_2) \\ \text{NaCl } (0.1\,x_2) \end{matrix} \qquad (1)$$

$$\text{HCl } (0.1) \Big| \begin{matrix} \text{NaCl } (0.1\,x) \\ \text{HCl } (0.1-0.1\,x) \end{matrix} \qquad (2)$$

were measured. The total concentration on each side of boundary was kept at 0.1 normal. X represents the molal proportion of sodium chloride to the total electrolyte. These junctions appeared to be of interest because of their bearing, in general, on modern theories of electrolytic solutions and, in particular, on the validity of the transference and ion-conductance relations found by MacInnes. The measurements were made with a "flowing" junction between the solutions, using a modification of the apparatus of Lamb and Larson.[1]

It has been shown by MacInnes [2] that the chloride ion conductance is the same, at a given concentration, in solutions of the alkali chlorides and hydrochloric acid; that is, $N_{Cl}\lambda = \text{constant}$ where N_{Cl} is

[1] Lamb and Larson, J. Am. Chem. Soc., 42, p. 229; 1920.

[2] MacInnes, J. Am. Chem. Soc., 43, p. 1217; 1921; MacInnes and Cowperthwaite, Trans. Faraday Soc., 23, p. 400; 1927.

the chloride ion transference number and λ is the equivalent conductance of any such solution. In other words, the conductance of the ion constituents is an additive property for such solutions at a given concentration. This was found to hold accurately within the concentration range of 0.01 to 1.0 normal. MacInnes [3] and Braley and Rippie [4] have shown that transference data on mixtures of these chlorides are in accord with the same simple additivity of conductances of the ion constituents. The transference numbers of the ions in the mixtures can, therefore, be expressed in terms of the transference numbers in solutions of the pure salts at the same concentration as the total concentration of the mixture. In the case of a mixture of sodium chloride and hydrochloric acid the expression for the hydrogen ion transference number is

$$T_H = \frac{N_H(1-N_{Na})}{(N_H-N_{Na})+(1-N_H)/x}$$

where N_H and N_{Na} are the transference numbers of the hydrogen and sodium ions in the solutions of the pure salts each at the total concentration of the mixture, and x is the ratio of the number of mols of sodium chloride in the mixture to the total concentration. If the same relations are applied in the derivation of the formula for the potential difference across the boundaries between solutions of these mixed chlorides, as represented in (1), the result [5] is

$$E=\frac{R\ T}{F}\ 1n\ \frac{(1-N_{Na})-x_2(N_H-N_{Na})}{(1-N_{Na})-x_1(N_H-N_{Na})} \tag{3}$$

and for a junction of type (2), where $x_1=o$,

$$E=\frac{R\ T}{F}\ 1n\ \frac{(1-N_{Na})-x(N_H-N_{Na})}{(1-N_{Na})} \tag{4}$$

Formula (3) can be obtained from (4) by taking the difference between two expressions for E according to (4). For this reason only one measurement was made on a junction of type (1) to test the validity of the general relation, and a series of determinations was made on junctions of type (2).

A similar series of measurements, incidental to another investigation, has been carried out by Ferguson and Bacon [6] using a "static" junction and calomel electrodes with cells of the type

$$\text{Hg; HgCl, satd. KCl} \left| \text{HCl}(0.1) \right| \begin{matrix}\text{NaCl } (0.1\,x)\\ \text{HCl } (0.1-0.1\,x)\end{matrix} \left| \text{satd. KCl, HgCl; Hg} \right.$$

[3] MacInnes, J. Am. Chem. Soc., **47**, p. 1922; 1925.
[4] Braley and Rippie, J. Am. Chem. Soc., **49**, p. 1493; 1927.
[5] MacInnes, J. Am. Chem. Soc., **48**, p. 2831; 1926.
[6] Ferguson and Bacon, J. Am. Chem. Soc., **46**, p. 1921; 1927.

II. APPARATUS

The cell used is shown diagrammatically in Figure 1. It includes a junction of the type described by MacInnes and Yeh.[7] A junction of this type in all probability gives a "mixture" boundary; that is, in the thin layer between the two solutions the composition changes progressively from that of the one solution to that of the other, the total concentration of electrolyte, however, remaining the same at all points in the junction. A mixture boundary is assumed in deriving equations (3) and (4).

A thermostat of about 85 liters capacity, containing well-stirred liquid petrolatum and provided with a mercury contact regulator and a heater, held the temperature constant at $25° \pm 0.05°$ as measured

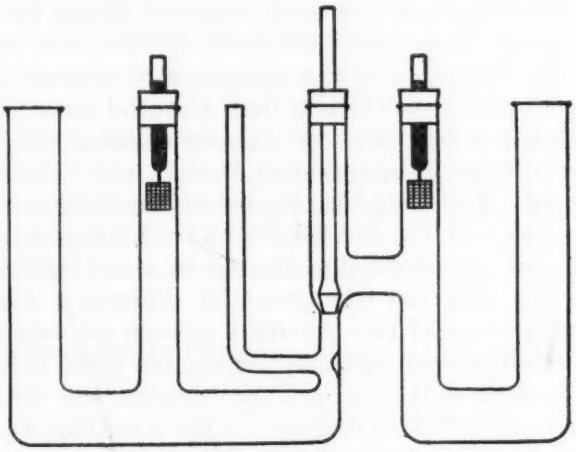

FIGURE 1

with a calibrated thermometer graduated in 0.2° divisions and read with an attached magnifying glass.

The electromotive force determinations were made with a Leeds & Northrup type K potentiometer and a recently certified standard cell.

III. MATERIALS

Hydrochloric acid of constant boiling point was prepared, and its composition was checked by determining the chloride as AgCl. The two chloride analyses agreed to 1 part in 4,000.

The sodium chloride was purified by precipitation with hydrochloric acid gas from a filtered solution of the c. p. salt. The salt thus obtained was dried and heated in a platinum dish until it began to fuse.

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[7] MacInnes and Yeh, J. Am. Chem. Soc., 43, p. 2563; 1921.

The solutions were made up by weighing out portions of the stock solution of the acid and of the salt and adding the proper weight of water to make the solutions contain 0.1 equivalent of chloride to 1,000 g of water. All weights were reduced to vacuum.

1. SILVER-SILVER CHLORIDE ELECTRODES

Contrary to the report of Randall and Young,[8] electrolytically plated silver-silver chloride electrodes on a base of platinum were found to be satisfactory and reproducible as judged by intercomparison. They were prepared as follows: To start with, eight pieces of platinum gauze 1.3 cm square, welded to platinum wires sealed into glass tubes,[9] were coated with silver from a solution of potassium silver cyanide and soaked for 10 days in changes of distilled water. The silver thus deposited was never removed during the course of the work. These silver electrodes were divided into two sets of four each. The day previous to a measurement each set was coated electrolytically with silver chloride from a central larger silver-silver chloride electrode of the same type in a crystallizing dish filled with solution of the same composition as that in which the electrodes were to be used. Following this, the central electrode was removed, the solution discarded, the dish filled with fresh solution of the same composition, and the electrodes allowed to stand in this solution overnight. The next day the potential differences between the different combinations of two electrodes in each set were measured. Of the 117 combinations compared during the work only one pair differed by as much as 0.1 mv, and the variation was usually of the order of magnitude of 0.02 to 0.03 mv. After a run the silver chloride on the electrodes was converted into silver by electrolysis, chloride being plated on the central larger electrodes. The silver electrodes thus re-formed were then ready for conversion into silver-silver chloride electrodes in the proper solutions, as before.

IV. EXPERIMENTAL RESULTS

With the flowing junction apparatus used, a rate of flow of 5 to 10 drops a minute was found to give a liquid junction potential which did not vary more than about 0.1 mv during the time taken (from one to two hours) for a determination. Readings were made every five minutes and the results reported here are their averages.

The values of N_{Na} and N_H applied in Equations (3) and (4) were 0.3864 and 0.8320, respectively.[10] Substitution of these values in (4) gives the equation

$$E=0.05915 \log_{10} (1-0.7262\, x) \text{ at } 25° \qquad (5)$$

[8] Randall and Young, J. Am. Chem. Soc., **50**, p. 989; 1928.
[9] MacInnes and Beattie, J. Am. Chem. Soc., **42**, p. 1132; 1920.
[10] Smith and MacInnes, J. Am. Chem. Soc., **47**, p. 1009; 1925.

Table 1 shows the measured values, including the value, marked with an asterisk, of MacInnes and Yeh for the junction.

TABLE 1.—*Potential differences across the junctions of 0.1 N hydrochloric acid and 0.1 N mixtures of hydrochloric acid and sodium chloride*

No.	x	Measured emf	Calculated emf	Difference
		mv	*mv*	*Per cent*
1	0.2346	4.75	4.80	−1.1
2	.5050	11.85	11.73	+1.0
3	.6142	15.12	15.17	−.33
4	.7518	20.17	20.28	−.55
5	.8931	26.80	26.87	−.26
6	.8997	27.18	27.14	+.15
7	.9400	29.41	29.48	−.23
8	1.000	33.17	33.28	−.33
	* 1.000	* 33.09	33.28	−.57

Measurement by MacInnes and Yeh.

$$\text{HCl (0.1)} \mid \text{NaCl (0.1)}$$

The latter result is the average of three determinations yielding 33.07, 33.13, and 33.07 mv and is in good agreement with the corresponding value found in this work, which is the average of two determinations yielding 33.166 and 33.171 mv. The percentage differences between measured and calculated values are given in the last column.

TABLE 2.—*Measurements by Ferguson and Bacon of the liquid junction potentials*

x	Measured emf	Calculated emf	Difference
	mv	*mv*	*Per cent*
0.04	1.05	0.76	+28
.1	2.04	1.94	+4.9
.4	8.23	8.82	−7.2
.8	20.97	22.35	−5.1
1.0	30.15	33.28	−10

The cell

$$\text{Ag; AgCl, } \begin{matrix}\text{HCl (0.07654)}\\ \text{NaCl (0.02346)}\end{matrix} \Big| \begin{matrix}\text{HCl (0.01003)}\\ \text{NaCl (0.08997)}\end{matrix} \text{, AgCl; Ag}$$

in which $x_1 = 0.2346$ and $x_2 = 0.8997$ was measured to test the general relation given by equation (3). The value found was 22.39 mv as an average of two runs which yielded the values 22.425 and 22.359 mv. If value No. 1 is subtracted from No. 6 in Table 1, it is seen that 22.43 mv is the liquid junction potential of this cell measured by difference in good agreement with the calculated value of 22.34 mv as well as with the direct determination.

The electromotive force values for similar "static" junctions reported by Ferguson and Bacon are shown in Table 2. Their cells

contained three liquid junctions, and in view of the 3 mv difference between their value for the simple junction

$$\text{HCl (0.1)} \mid \text{NaCl (0.1)}$$

and the value given by MacInnes and Yeh, which was confirmed in the present work, it is probable that definite reproducible measurements can not be made by their method.

V. DISCUSSION

Evidence has been given by Harned [11] that the activity of the chloride ion is the same, within the precision limits of liquid-junction measurements, at any one total electrolyte concentration in different mixtures of hydrochloric acid with the alkali chlorides. The silver-silver chloride electrode potentials are, therefore, balanced in the cell within the accuracy of these measurements, and the measured electromotive force is thus the potential difference across the liquid junction.

The hypotheses involved in the calculation of these liquid-junction potentials by equations (3) and (4) are:

(*a*) The same degree of dissociation of each chloride in each mixture.

(*b*) Substantially constant chloride ion activities in univalent chloride mixtures of the same (dilute) total concentration. This, as Bronsted [12] has pointed out, can be strictly true only in very dilute solutions.

(*c*) The constancy of the product $T_{Cl}\lambda$ in each such mixture. Included in (*a*) is the absence of complex formation. Substantially complete dissociation is consistent with (*a*). The agreement of the calculated with the measured potential differences is evidence for the validity of these hypotheses, at least for dilute mixtures of univalent chlorides, within the precision limits of these determinations.

VI. SUMMARY

The potential differences across liquid junctions of the types

$$\text{HCl (0.1)} \left| \begin{matrix} \text{HCl } (0.1-0.1x) \\ \text{NaCl } (0.1\,x) \end{matrix} \right.$$

$$\begin{matrix} \text{HCl } (0.1-0.1\,x_1) \\ \text{NaCl } (0.1\,x_1) \end{matrix} \left| \begin{matrix} \text{HCl } (0.1-0.1\,x_2) \\ \text{NaCl } (0.1\,x_2) \end{matrix} \right.$$

were measured using a flowing junction and silver-silver chloride electrodes. In contrast to the static-junction measurements on such boundaries, as made by Ferguson and Bacon, these flowing junction

[11] Harned, J. Am. Chem. Soc., **42**, p. 1808; 1920.
[12] Bronsted, J. Am. Chem. Soc., **45**, p. 2898; 1923.

determinations give reproducible values for the liquid-junction potentials which can be accurately computed from the formula

$$E=\frac{RT}{F}\,1n\,\frac{(1-N_{Na})-x_2\,(N_H-N_{Na})}{(1-N_{Na})-x_1\,(N_H-N_{Na})}$$

where x_1 and x_2 represent the molal proportions of sodium chloride to the total electrolyte concentration, and N_{Na} and N_H are the cation transference numbers in solutions of the pure electrolytes at the same concentration as the total concentration of the mixture.

WASHINGTON, December 8, 1928.

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THE ACCURATE DETERMINATION OF THE GASOLINE CONTENT OF NATURAL GAS AND THE ANALYTICAL SEPARATION OF NATURAL GASES BY ISOTHERMAL FRACTIONAL DISTILLATION

By Martin Shepherd

ABSTRACT

This paper describes a method for the accurate determination of gasoline in natural gas. The determination involves a special separation of the natural gas by fractional distillation at low temperatures and pressures. A recombination of the resultant fractions is made in such a way that it is possible to determine the maximum amount of hydrocarbon condensate present in the original gas which possesses any given vapor pressure at any given temperature. Special forms of apparatus are used for separating the higher boiling constituents and determining their liquid volume to 0.001 ml. Apparatus and procedures are described in detail, analytical results given, and a direct comparison made with existing field and laboratory methods. The analytical separation of natural gases and their commercial condensates is also discussed. The paper as a whole is intended to be a simple instruction book for those who wish to engage in such work.

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I. NEED FOR AND SCOPE OF THE METHOD

Of the various existing field and laboratory methods for the determination of natural gasoline in natural gas[1] three deserve mention. They are the compression-cooling method, the oil-absorption method, and the charcoal-adsorption method. There are many variations of these three methods, and the individual operator is apt to introduce modifications suitable to his peculiar needs. It is very difficult to obtain satisfactory agreement between the methods, and apparently it is almost equally difficult for different operators to obtain satisfactory analytical checks by use of the same method.

The Natural Gas Association of America recognized this discordant state and appointed a committee to study the problem and formulate standard methods of test. The committee's investigation led to a partial and tentative standardization of the three methods already mentioned[2] and a critical study of their accuracy which the present paper will report in part. This study has clearly shown the need of a reference or umpire method for the determination of natural gasoline.

[1] For a description of these methods see Burrell, Recovery of Gasoline from Natural Gas, ch. 10, A. C. S. Monograph Series, Chemical Catalog Co., New York.

[2] Code of the Natural Gas Association of America, No. 1. Report of the Committee on Standard Testing for Gasoline. The Natural Gas Association of America, 908 Oliver Building, Pittsburgh, Pa.

The method here proposed is intended for reference, standardization, and investigational work. The relatively complicated equipment and procedures required make the method unsuited for routine field testing or ordinary plant control. It possesses its own distinct value, however, whenever new processes are to be investigated or actual plant efficiencies determined. It may be used to study and standardize ordinary methods of plant control or resorted to in case of umpire decisions involving questions of the true natural gasoline content of natural gases. It is the only known method capable of analytically separating natural gases and quantitatively determining their constituents. As such, it is being successfully used by a number of commercial laboratories which have been in touch with the present work during the past several years.

II. DEVELOPMENT OF A DEFINITION OF THE TERM "NATURAL GASOLINE" CONTENT OF NATURAL GAS

In order to develop an analytical method for the quantitative determination of some one substance in a mixture of other substances, it is obviously necessary to define clearly the nature of the one substance sought. Strangely enough, this usually simple requirement has presented a most perplexing problem in the present instance, for entire agreement has never been reached in the natural-gas industry as to just what is meant by the term "gasoline," or more particularly "natural gasoline," since we are directly concerned with a product of that name extracted from natural gas. It is generally agreed that "natural gasoline" consists of a mixture of hydrocarbons which may be condensed from natural gas, and that this condensate should be commercially manageable; that is, capable of safe transportation from the place of its origin to wherever it may find its final use—usually the blending with refinery and cracked "gasolines." But just what the exact chemical composition of this condensate may be is a question which can not be answered. Because of the different character of natural gases from various fields, and because of the difference in local requirements of refiners, what is considered "natural gasoline" in Pennsylvania may not be "natural gasoline" in Texas, and a California or Wyoming "natural gasoline" may not be recognized as such in either of the first two localities. Nor, for that matter, does perplexity cease with the consideration of the geographical environment of this problematic compound. A perfectly respectable "natural gasoline" born of the winter months might find its reputation for sobriety entirely reversed during the hot days of summer. So it is that geographical and meterological conditions conspire to confuse the identity of the substance which we must determine by analysis without knowing just what it is we are to determine.

With this troublesome situation as a beginning, it may seem difficult to develop a definition of the term "natural gasoline" content. However, a workable definition, based on the two factors of chemical composition and vapor pressure, seems possible and desirable.

Vapor pressure becomes one criterion, since present Interstate Commerce Commission shipping regulations are formulated with respect to this property.[3] With an arbitrary classification of petroleum condensates once established on such a basis, the producer of natural gasolines must then be directly concerned with the vapor pressure of his product.

On the other hand, it is obviously possible to produce hydrocarbon condensates of an infinite variety of percentage compositions, all of which may possess an identical vapor pressure at some fixed temperature. Natural gas is composed largely of the saturated hydrocarbons, of which the proportion ordinarily making up the condensate called "natural gasoline" is of the order of magnitude of 1 or 2 per cent of the total gas. The vapor pressures of these components at once establish the fact that pentane and other hydrocarbons of the series of higher boiling points may be safely included as properly belonging to the condensate to be called natural gasoline. The further fact is evident that some butane may be included in such a mixture without exceeding the vapor pressure requirements. In practice small percentages of propane or even ethane are actually held in solution with the desirable components, although present developments in "stabilization," which include the use of a simple rectifying column, are tending to correct this error. It is apparent that small traces of propane will appreciably increase the saturation pressure of such a mixture and cause inexcusable "weathering" losses. Rafferty [4] and others have advanced interesting data to show the relative changes of vapor pressure caused by butane and propane present in condensates of pentane and higher boiling hydrocarbons. Whether or not these data are entirely correct, they certainly show the right trend.

From this simple consideration of vapor pressures it follows that for any one natural gas of definite composition there is a definite maximum amount of condensate, possessing a fixed vapor pressure (p) at some fixed temperature (T), which can be extracted from this gas, and that when this maximum yield is obtained the composition of the condensate is perfectly definite. The percentage composition and volume of this maximum amount of condensate will depend entirely on the original composition of the gas and the arbitrary saturation pressure and temperature selected. In the case of a "natural gasoline" this condensate will contain all of the pentane and hydro-

[3] Bureau of Explosives, Pamphlet No. 9, pp. 50–51, published December, 1922, by Bureau of Explosives, 30 Vesey Street, New York, N. Y.

[4] J. A. Rafferty, Nat. Petroleum News, p. 35; Apr. 25, 1923.

carbons of higher boiling points occurring in the original gas and, in addition, as much normal butane as may be incorporated without exceeding the fixed vapor pressure (p) at the temperature (T). It will include no isobutane, propane, or hydrocarbons of lower boiling points. Such a condensate is a definite substance which can be determined quantitatively.

Accepting this concept as a reasonable basis of identification, we may then define the natural gasoline content as the hydrocarbon condensate derived from natural gas which is composed of the total percentages of pentane plus higher boiling hydrocarbons occurring as vapors in the natural gas, plus a sufficient percentage of normal butane to cause the total condensate to possess a saturation pressure (p) at a temperature (T).

The method described in this paper may be used to determine this natural gasoline content. The assignment of desirable values for (p) and (T) is not attempted, this matter being in the hands of the industry. Rather, in the present work, (p) was determined over a relatively wide range with (T) held constant, so that it is possible to compute the amount of this maximum condensate possessing any convenient saturation pressure. These data are useful in connection with blending or other special problems of the industry. Further, (p) may be determined for various values of (T). The value 100° F. was used for (T) in the present work, being selected with reference to shipping regulations. If it is desired to accept the corresponding limiting figure of 10 lbs./in.^{2} for vapor tension, we are in a position to definitely state the amounts of "natural gasoline," and analogously those of "casing-head gasoline" (not over 20 lbs./in.^{2} at 100° F.) and "liquified petroleum gas" (over 20 lbs./in.^{2} at 100° F.) in the natural gas.

III. PRINCIPLE OF THE ANALYTICAL METHOD

With the development of a definition for the term "natural gasoline," it is possible to establish an analytical method for the determination of the natural gasoline content of any natural gas. The analysis will obviously require that the natural gas be separated into three fractions:

1. Isobutane, propane, and hydrocarbons of lower boiling points, together with nitrogen and traces of oxygen, carbon dioxide, and helium, if present.
2. Normal butane.
3. Pentanes and hydrocarbons of higher boiling points.

Fractions 1 and 2 may be measured in the vapor phase. Fraction 3 may be determined in the vapor phase by difference from the original sample, and further measured directly in the liquid phase by means of especially designed apparatus. The vapor pressure of fraction 3 may then be measured at some fixed temperature.

Measured increments of fraction 2 may be recondensed into fraction 3, the increase of vapor pressure at the fixed temperature being noted for each addition. In this manner the percentage of hydrocarbon condensate present in the original gas may be plotted against its vapor pressure at any fixed temperature. Furthermore, the maximum amount present in the original gas which will possess the vapor pressure noted at the fixed temperature is given by this plot, since the composition of this condensate represents the hydrocarbons in direct order of their boiling points from high to low. A curve plotted from such data discloses this maximum percentage for any desired vapor pressure at the fixed temperature. The percentages may be expressed in the vapor phase and a factor applied to translate these to gallons per million cubic feet, or they may be expressed directly in the liquid phase in the same unit. It will be shown later that the two methods check within the accuracy demanded by natural-gas engineers.

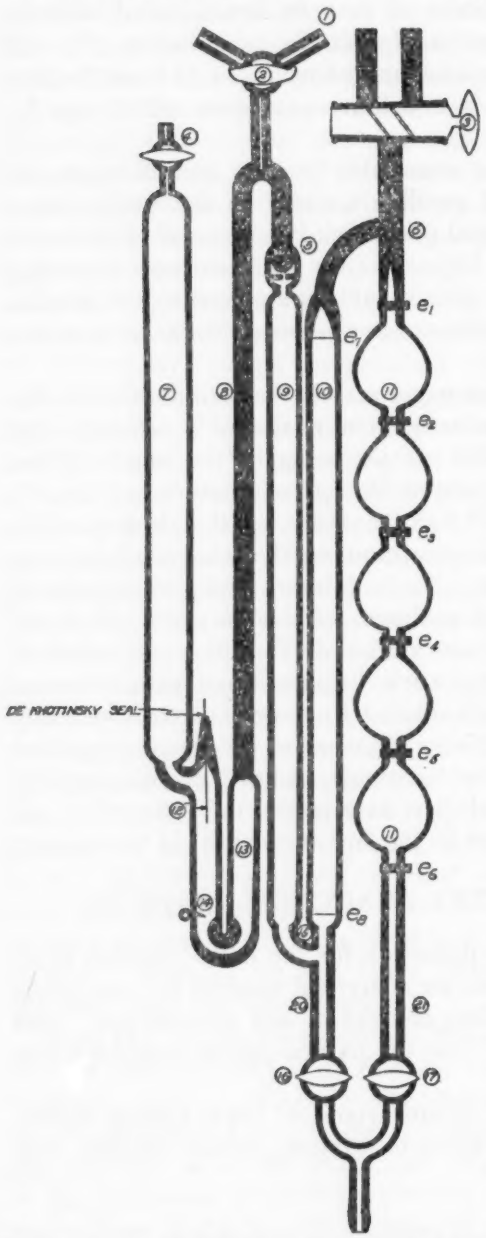

FIGURE 1.—*Gas burette with vernier scale and without gas connection to compensator (substitute for B_2 of Figure 10)*

In order to separate the natural gas into the fractions noted, it is necessary to employ a method of fractional distillation at low temperatures and pressures. The method here used is a development of that of Shepherd and Porter.[5] Several inac-

[5] Shepherd and Porter, Ind. Eng. Chem., 15, p. 1143; 1923.

curacies of the former method are corrected and the apparatus modified so as to effect more efficient separations and increase the ease of manipulation.

IV. APPARATUS

The apparatus consists of units for measuring gas and liquid volumes, manometers for measuring saturation pressures, pipettes for absorption and combustion analyses (if desired), pumps for the transference of gas volumes, and a system of distilling bulbs for effecting the separation of the gas sample. These must be assembled to form one single unit, the various parts of which are interconnected by fused glass joints. Auxiliary apparatus consists of suitable devices for controlling and measuring low temperatures, liquid-air containers, and one or more mechanical vacuum pumps, such as those employing gears or eccentric cams immersed in oil.

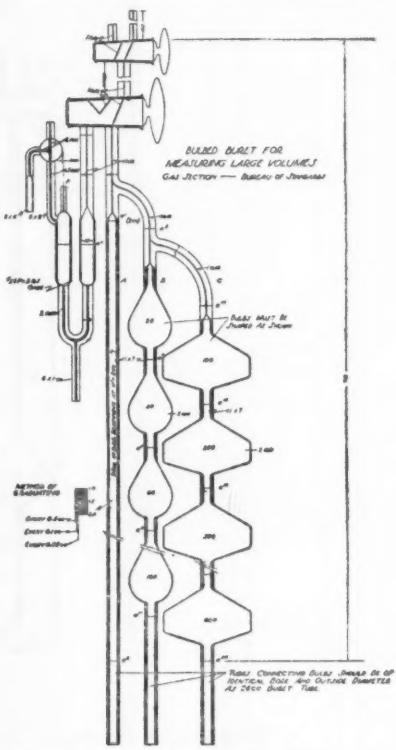

FIGURE 2.—*Gas burette, B_2 of Figure 10*

1. GAS BURETTES

The burette[6] used in the present investigation was one designed without gas connection to the compensator. It is of the bulbed type, and measurements of fractional volumes are made on a side arm provided with a scale and vernier. The glass parts are illustrated in Figure 1. The accuracy is 0.01 ml or better. It was used in connection with a calibrated bulb of 1 liter capacity in order to lessen the number of volume measurements required.

A somewhat preferable form for the present work is shown in Figure 2. It is a bulbed burette of large capacity, capable of measuring both the original sample and any fraction thereof at one step. This obviously decreases the time required for a determination. The drawing indicates the construction of the burette alone. A compensator should be connected to the manometer.

[6] This burette is described in B. S. Sci. Paper No. 559, A Burette for the Accurate Measurement of Gas Volumes without Gas Connection to a Compensator, by E. R. Weaver and Martin Shepherd.

2. LIQUID BURETTE

A special weight burette [7] was used for the measurement of the pentane and higher boiling hydrocarbons. (Fig. 3.) Determinations may be made with an accuracy of 0.001 ml.

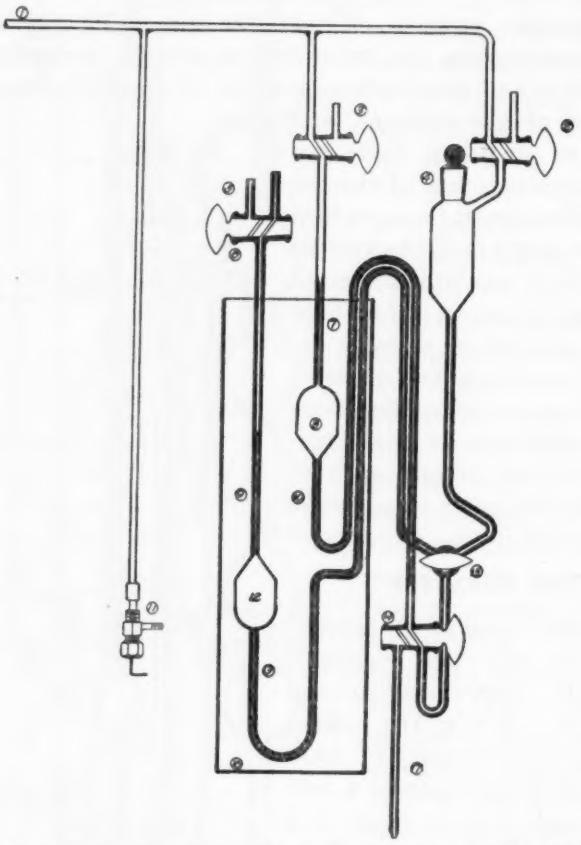

FIGURE 3.—*Burette for the measurement of small liquid volumes, B_1 of Figure 10*

3. PIPETTES FOR GAS ANALYSIS

While any suitable type may be used, the preferred forms are the Weaver-Ledig combustion pipette [8] and the Dennis-Friedrichs absorption pipette.[9] These are unnecessary if it is not desired to make a complete analysis of the natural gas, which involves the estimation of nitrogen in a nitrogen-methane fraction.

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[7] The burette and its operation are described in detail in B. S. Sci. Paper No. 555, A Weight Burette for the Micromeasurement of Liquid Volumes, by Martin Shepherd.

[8] J. Ind. Eng. Chem., **12**, p. 368; 1920.

[9] Dennis, Gas Analysis, Macmillan Co. of New York, p. 81; 1918.

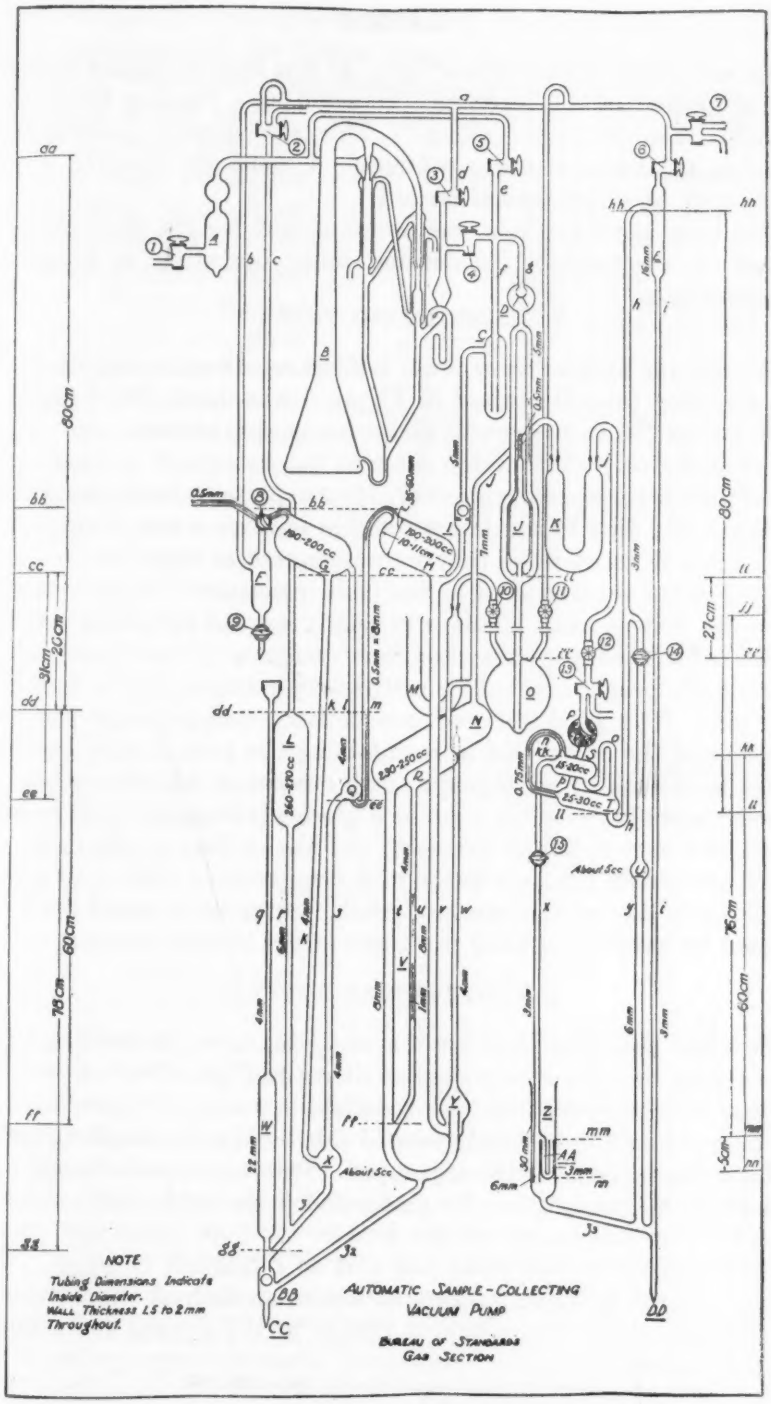


FIGURE 4.—*Automatic Töpler pump, V_2 of Figure 10*

4. PUMPS

An automatic Töpler pump [10] (fig. 4) was used to collect nitrogen and a portion of the methane. It acted as a backing pump to a Stimson mercury vapor pump.[11] This arrangement permits high speed in the transfer of gas volumes. A manually operated Töpler pump may be substituted if desired.

The transference of gas was accomplished for the most part by means of a system of condensing bulbs operating at liquid air temperatures.

5. DISTILLING TUBES

(*a*) For the separation of lower boiling constituents and final cuts the distilling tube illustrated in Figure 5 was used. It is provided with a sealed-in thermocouple and a barometric manometer. (Indicated in sketch.) The cotton filter at the bottom of this tube prevents the mechanical carrying over of frozen particles in the gas stream. Without this filter it was found possible to carry water through four such tubes in series when they were immersed in liquid air.[12]

(*b*) For the separation of higher boiling constituents the rectifying tube (fig. 6) was used. This is in reality a small rectifying column. It is filled with copper balls of uniform diameter (about 3 mm), which provide the proper spacing for satisfactory reflux action in a tube of this size. The good thermal conductivity and possibly the heat capacity of the copper aid in maintaining the temperature gradient, which is effected by supplying a small current to a nichrome heating element wound about the tube in a gradually opening helix as indicated, the heat so added balancing the loss of heat to the liquid air which surrounds the tube but is held from contact with it by an air bath. Any desired temperature gradient may be imposed upon the column by properly spacing the turns of the heating element.

6. TEMPERATURE CONTROL

This has been described for the rectifying type of distilling tube. The copper cylinder constructed as shown in Figure 7 provides satisfactory temperature control for the distilling tube of Figure 5. The cylinder is bored to fit snugly around this tube, and a smaller parallel well accommodates a thermocouple. The whole unit hangs suspended in a Dewar tube, the perforated plate at the top providing support over the mouth of the Dewar. A fiber collar secures the copper cylinder to this plate and acts as a thermal insulator. The bottom of the cylinder projects to within an inch of the bottom of the Dewar tube. The whole is cooled to the desired temperature

[10] E. R. Weaver and Martin Shepherd, J. Am. Chem. Soc., **50**, p. 1829; 1928.

[11] Stimson, J. Wash. Acad. Sci., **7**, p. 477; 1917.

[12] The distillation of glycerine through a common U tube at liquid hydrogen temperatures has also been observed by C. W. Kanolt at the Bureau of Standards.

with liquid air, and the slow vaporization of a small amount of liquid air at the bottom of the Dewar tube, combined with the high heat capacity of the copper block, is sufficient to hold the temperature to within 0.5° of any desired value over the range −160° to −80° C. during the time consumed by an average distillation. Further temperature adjustment is effected by the occasional addition of small amounts of liquid air through the perforated top plate. The thermal conductivity of the copper block is quite sufficient to maintain the desired uniformity of temperature under these conditions.

The device has been used for several years and replaces the cooled hydrocarbon bath often used for this purpose. The latter presents a distinct fire hazard, since the confining Dewar tube may explode at any time and in so doing practically atomize the liquid contents, which may in turn ignite from any accidental source, possibly even a static spark from the disrupting glass of the Dewar tube itself. If a liquid bath is preferred, a nonflammable mixture, such as described by Kanolt,[13] may be used.

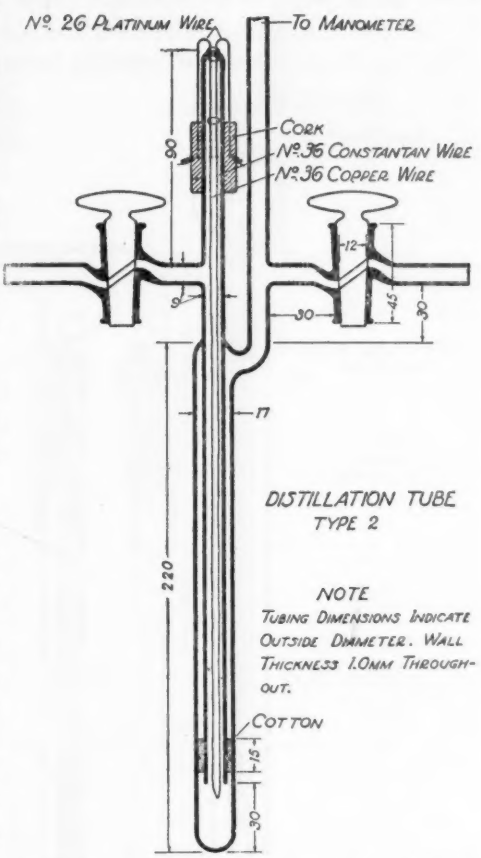


FIGURE 5.—*Plain distillation tube, II–V of Figure 10*

Condensing temperatures of approximately −210° C. are obtained by boiling liquid air under reduced pressure.[14]

Temperatures are measured by copper-constantan couples made from carefully calibrated No. 36 wire used in connection with a pre-

[13] B. S. Sci. Paper No. 520, Nonflammable Liquids for Cryostats, by C. W. Kanolt, or International Critical Tables, **1**, p. 61.

[14] The operator who may not be familiar with the handling of liquid air will find an excellent description of this technique given by Claude in his book, Liquid Air, Oxygen and Nitrogen (translated by Henry E. P. Cottrell, J. and A. Churchill, London, 1913, Pt. III, Ch. VIII, p. 202). This author describes not only the storage and manipulation of liquid air, but also gives a very interesting account of a number of experiments based upon its unusual physical and chemical properties.

cision potentiometer. When making vapor pressure measurements, temperatures were measured by a multiple couple.

Dewar tubes of approximately 1-pint size are ordinarily used for cryostat-bath containers, except for the rectifying type of distilling tube, which requires a larger size (approximately 1 quart). Six-pint Dewar flasks are convenient for the laboratory storage of liquid air. If the liquid air is to be shipped or transported to the laboratory from any distance, 15 or 25 liter metal containers are recommended. These maintain their own insulating vacuum by means of a charcoal cartridge held at the temperature of the liquid air. They are provided with a long, narrow neck, so that conduction down the metal is not a serious factor.

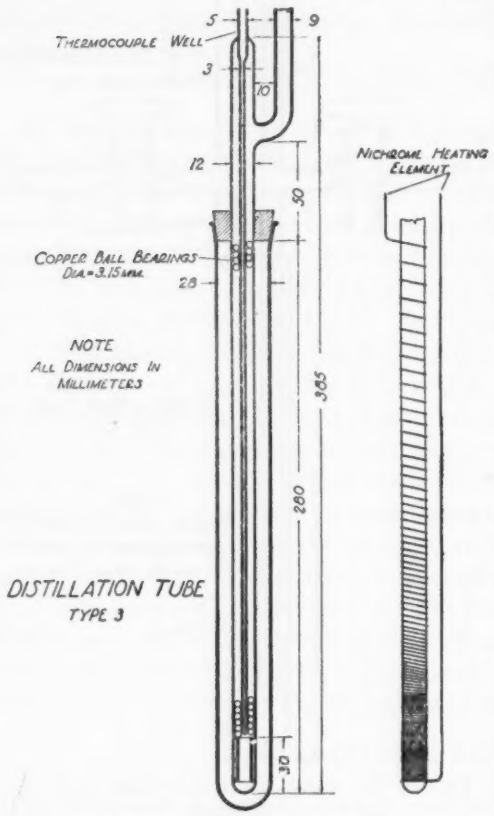


FIGURE 6.—*Rectifying distillation tube, tube I of Figure 10*

7. DIFFERENTIAL MANOMETER

A simple differential manometer for the determination of the purities of distillates is illustrated in Figure 8. It is not shown in the assembly drawing which follows, but should be connected to the distillation train at a point just beyond tube V and in the same line as bulbs C_3–C_5. (See fig. 10.) Stopcocks *1* and *2* of the manometer serve to open or close bulbs B_1 and B_2 to this portion of the distillation train. The manometer M is filled with clean mercury, and the levels are read by means of the hollow micrometer screws A_1 and A_2. These are constructed and calibrated exactly like a standard micrometer gauge, except that they are made hollow to accommodate the arms of the manometer to which they are cemented. The verniers read to 0.01 mm, and repeated trials have shown that readings of the position of the mercury menisci may be made with this precision. A diffused light is placed back of the manometer, and this

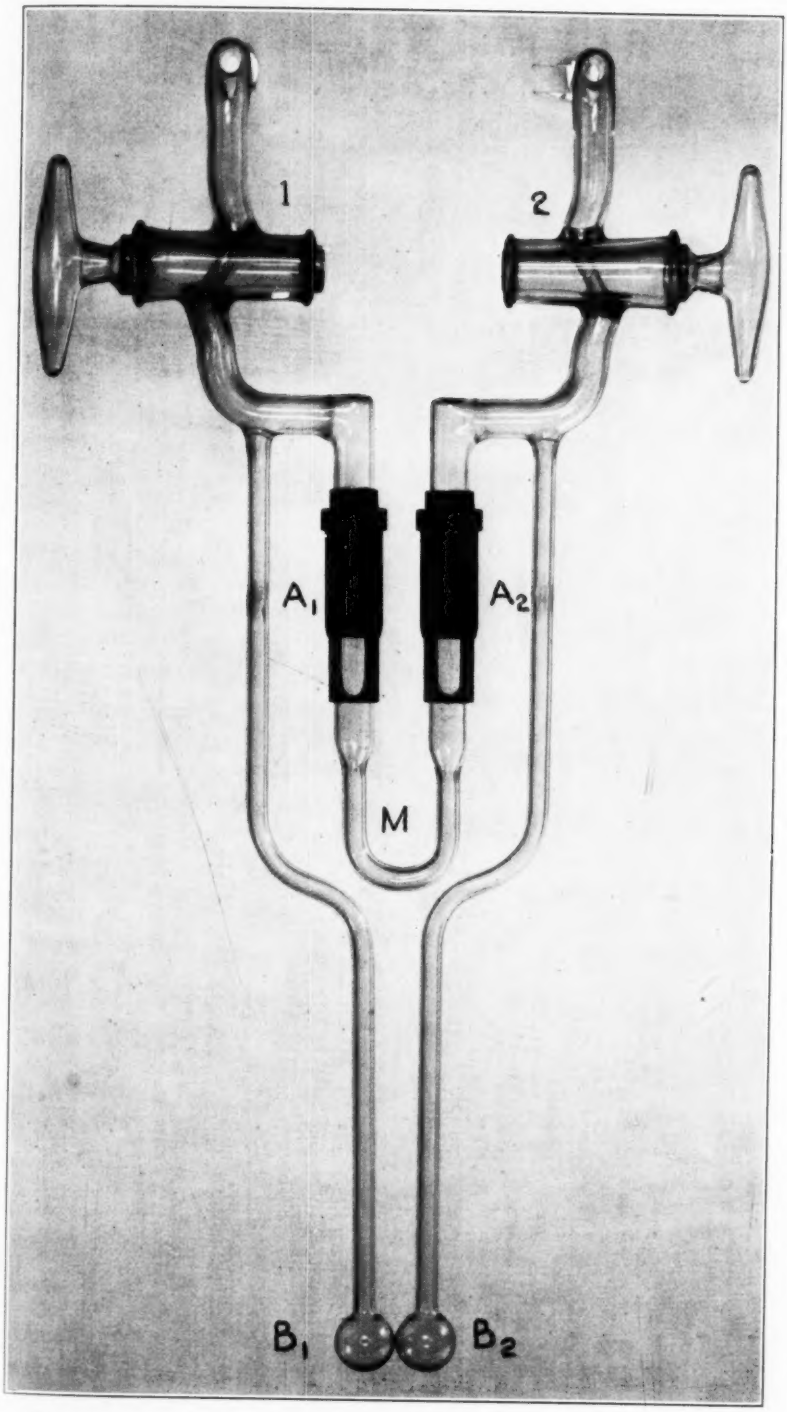
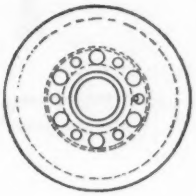


FIGURE 8.—*A differential manometer for measuring the purities of distillates*

is screened so that only the exposed portions of the glass arms within the slits formed by the micrometer casings are illuminated. The screw collar is adjusted to form an interference pattern at the top of the meniscus.

8. AUXILIARY VACUUM PUMPS

One or more oil-immersed gear or eccentric cam vacuum pumps are required. Three is a convenient number, although one can be made to perform all the necessary work. If three are used, one should provide reduced pressure over the liquid air baths; a second should be used as a backing pump for the mercury vapor pump; and a third connected to the various mercury reservoirs to raise the large volumes of mercury they contain.



9. STOPCOCKS

Since the procedure requires operation in part at very low pressures, it is necessary to eliminate all rubber connections and use only fused glass joints. The stopcocks located in parts of the apparatus subjected to high vacuum present sources of potential leaks and must, therefore, be very carefully ground. It has been found best to use simple cocks of the so-called "2-way" type rather than "3-way," T, or 120° cocks. A hollow-blown key ground to the so-called "mirror finish," of the dimensions shown in Figure 9 (*A*), is quite dependable. These should be lubricated with a grease similar to the "high vacuum" type described by Shepherd and Ledig.[15] With such high-grade cocks suitably lubricated, no difficulty has been experienced in maintaining high vacuum over long periods.

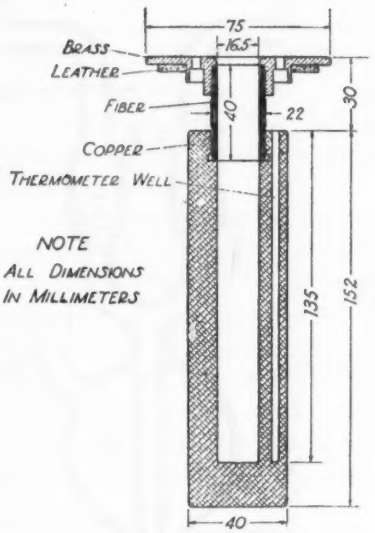


FIGURE 7.—*Temperature control unit for plain type distillation tube*

Some investigators prefer a mercury shut-off rather than a stopcock for high vacuum apparatus. A convenient design is shown in Figure

[15] Rubber Stopcock Lubricants for High Vacuum and Other Uses, by Martin Shepherd and Paul Ledig Ind. Eng. Chem., **19**, p. 1056; 1927.

9 (*B*). It has the advantage over the ordinary mercury shut-off of functioning over wide-pressure variations and at the same time presenting a compact unit that requires little space in the assembly of a large apparatus.

The outlets O_1 and O_2 are fused into the line where the gas flow is to be interrupted. Mercury from the reservoir *R* discharges into the U tube when pressure is applied through the air inlet of the auxiliary needle valve *V*. This mercury is withdrawn by connecting *R* to a

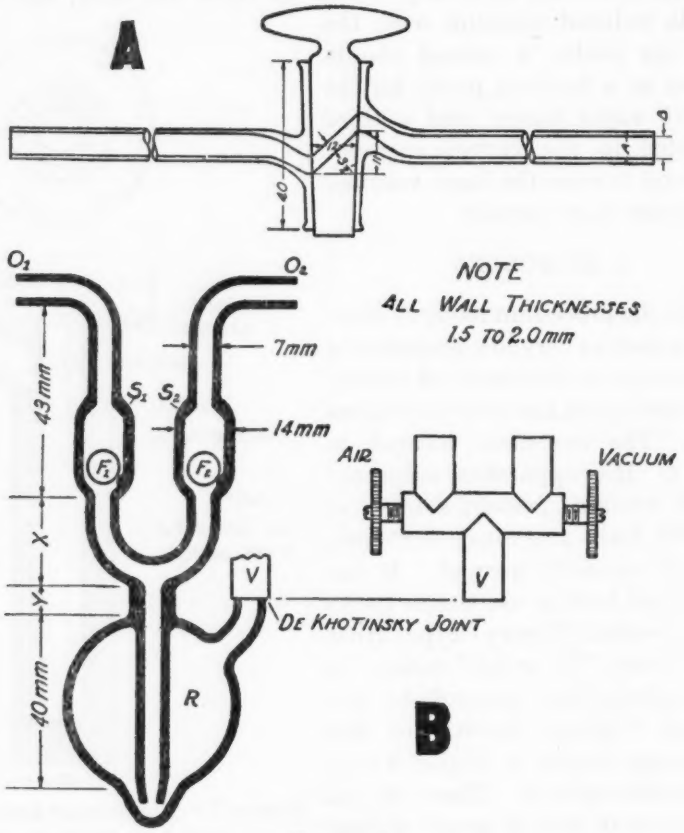


FIGURE 9

A, Stopcock for high vacuum work; *B*, mercury shut-off for high vacuum apparatus

vacuum line through the second outlet of the valve *V*. The floats F_1 and F_2 are solid glass balls ground spherical between rotating plates. They seat against 45° grindings S_1 and S_2, preventing mercury from being carried over into the apparatus. Such float valves have never been found to leak if properly ground.

The pressure applied at the air inlet of the needle valve determines the range over which the shut-off will operate. The dimensions of the glass U tube may be enlarged to suit the requirements of high vacuum work.

10. KIND OF GLASS

The unit may be constructed of Pyrex glass, although the author prefers a good grade of soft glass. The reasons for this are: (1) The tendency of Pyrex to "pinhole," even when carefully worked in an oxy-gas flame. This causes considerable trouble in high vacuum work, although it is quite possible to construct a satisfactorily tight apparatus of Pyrex. (2) The formation of an insulating film of gas between the liquid and the glass prevents the breaking of soft glass bulbs immersed in liquid air. No difficulty with breakage of this sort has been experienced when well-annealed soft glass bulbs were used, and Pyrex presents no real advantage in this respect in the present instance. The mercury vapor pump must, of course, be constructed from Pyrex stock, and this can be sealed into a soft glass unit with graded seals.

11. ASSEMBLY

(*a*) COMPLETE UNIT.—The apparatus is assembled as diagrammatically indicated in Figure 10. This drawing has been simplified with a key to lettering, so that the character of its individual parts are at once apparent. The detailed drawings of the various parts given in the preceding figures (1 to 6, inclusive) have been lettered so that direct reference can be made to the drawing of the assembly. The identity of each part is thus easily established.

(*b*) SIMPLIFIED UNIT.—The assembly drawing indicates the most convenient form of the apparatus and is strongly recommended in case extended work of this character is to be done. The apparatus has been considerably simplified for the use of commercial laboratories, however, and this simplified form has found favor with several laboratories which are investigating natural gasoline and refining problems. It is shown by two photographs (figs. 11 and 12), of which the former is the completely assembled unit and the latter a detailed view of the distillation train. A meter stick at the left of the photograph provides a scale.

For purposes of comparative study Figure 11 has been lettered to correspond directly to the lettering of Figure 10. The comparison will reveal a number of alterations appearing on the simplified apparatus. The distillation train remains unchanged except for the omission of a McLeod gauge. This simplification is not to be recommended except in cases where so-called "dry" natural gases are to be separated. The P_2O_5 drier is sealed as a T to the exit of the distillation train and may be turned to the line when the unit is standing idle. The mercury vapor pump is retained, but the system V_2RS_1 is substituted for the automatic Töpler pump. This system amounts to a manually operated Töpler pump without a barometric or float valve on the inlet. The bulb V_2 is of 1-liter capacity and acts not only as the backing pump for the mercury vapor pump but

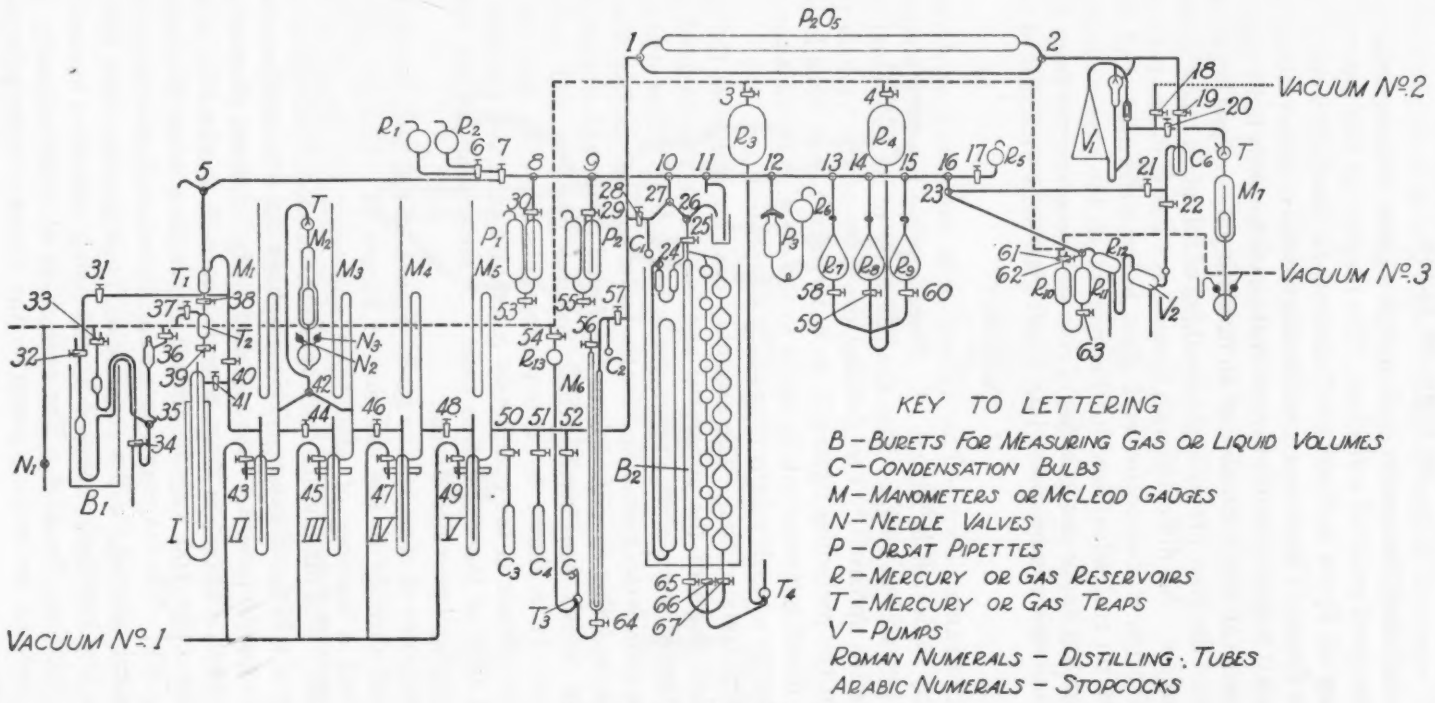

P_2O_5
VACUUM Nº 2
VACUUM Nº 3
VACUUM Nº 1
KEY TO LETTERING
B – BURETS FOR MEASURING GAS OR LIQUID VOLUMES
C – CONDENSATION BULBS
M – MANOMETERS OR McLEOD GAUGES
N – NEEDLE VALVES
P – ORSAT PIPETTES
R – MERCURY OR GAS RESERVOIRS
T – MERCURY OR GAS TRAPS
V – PUMPS
ROMAN NUMERALS – DISTILLING TUBES
ARABIC NUMERALS – STOPCOCKS

FIGURE 10.—*Assembly drawing*

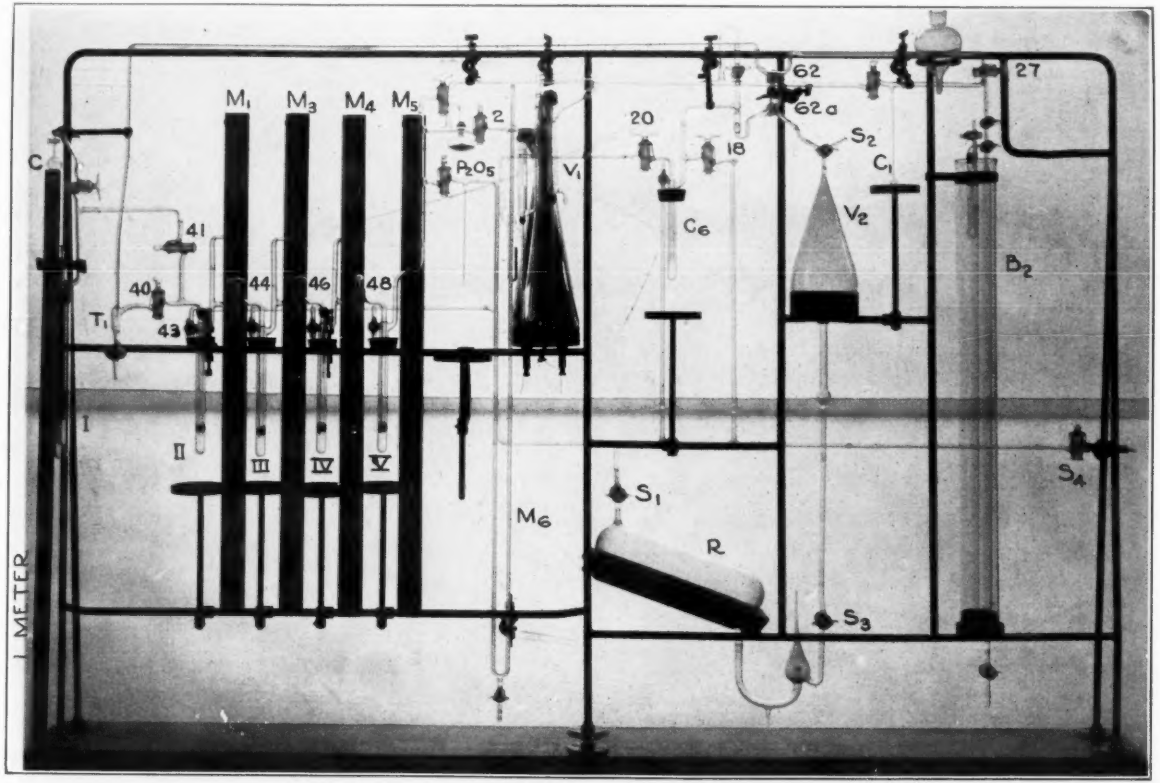


FIGURE 11.—*Assembly of simplified unit*

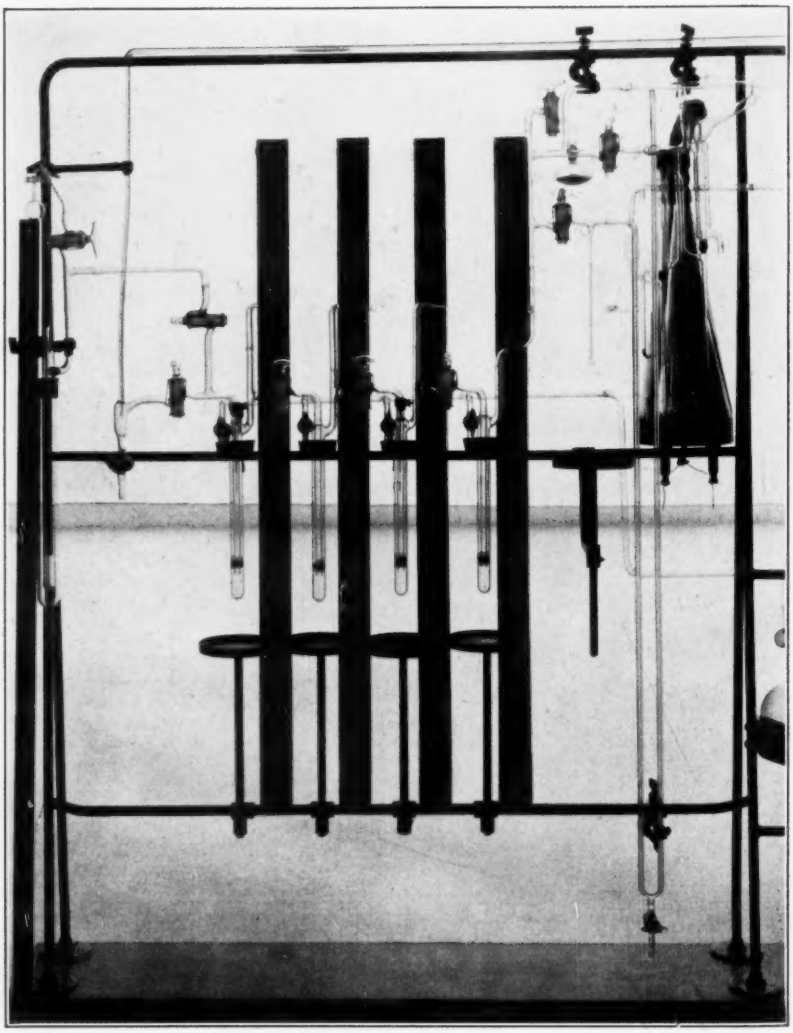


FIGURE 12.—*Detail of the distillation train of simplified unit*

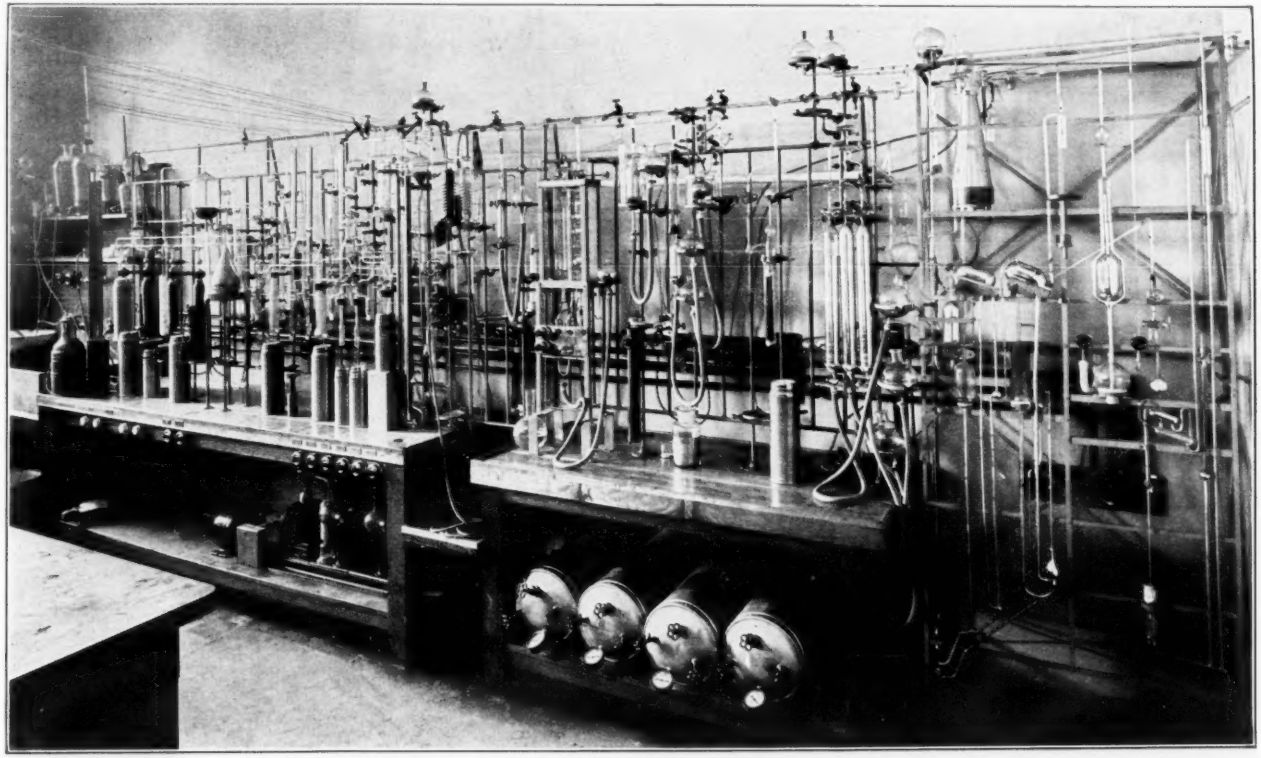


FIGURE 13.—*Complete assembly of experimental unit*

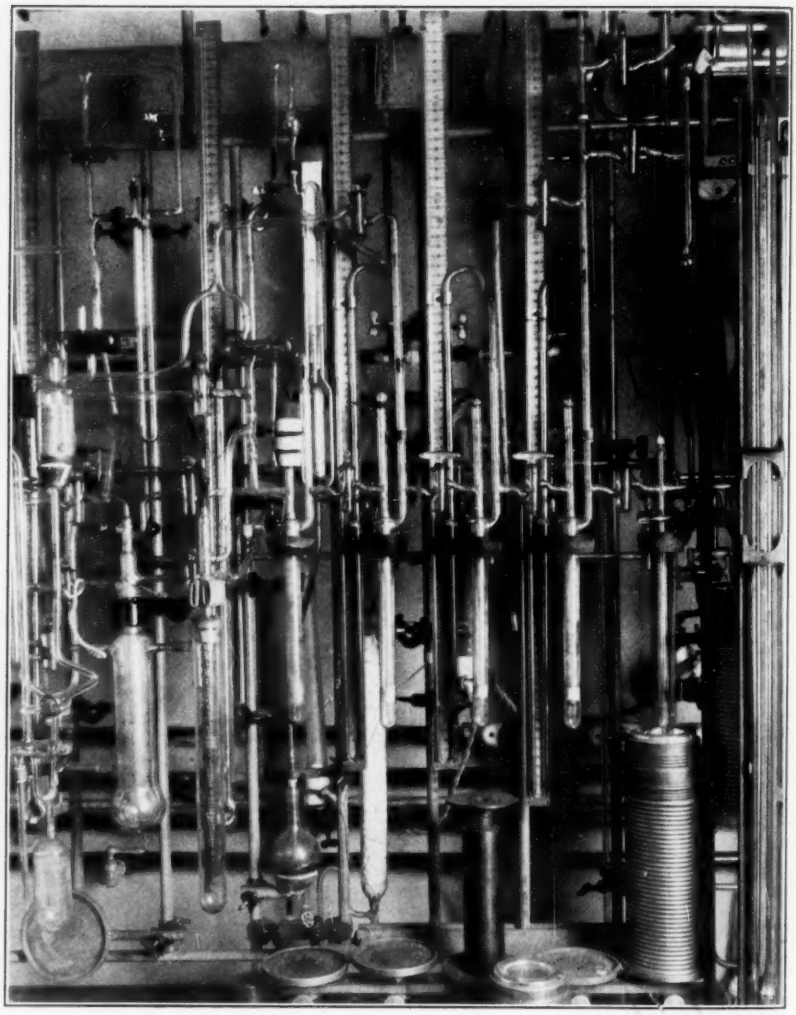


FIGURE 14.—*Detail of the distillation train of experimental unit*

also as the burette for the measurement of the original gas sample. When acting as the collecting pump, mercury from the reservoir R is forced into V_2 by pressure applied through the 3-way stopcock S_1, stopcock S_2 being turned to the atmosphere. When mercury has completely filled V_2, S_3 is closed, S_2 opened to C_6, and S_3 reopened with vacuum applied to R through S_1. The gas taken into V_2 is then forced directly into the burette B_2 by again applying pressure to R and adjusting stopcocks 62a, 62, and 27. Since the bulb V_2 is of very large capacity and has only C_6 and the connections to the pump V_1 to evacuate, a very few such operations are sufficient for initial evacuation or the removal of the nitrogen-methane fraction. All other pumping is done by direct condensation from the exit of the train to bulb C_1, stopcock 2 being closed and 28 opened for this purpose.

The simplified apparatus has no liquid or gas reservoirs and no combustion or absorption pipettes. The gas burette supplied is of the ordinary 100 ml compensated type, which increases the number of volume measurements of the various fractions. The liquid burette is omitted, determinations being made entirely in the vapor phase. A direct measurement of natural gasoline content is accordingly impossible. The vapor pressure manometer M_6 is retained. A bulb C for the introduction of liquid samples has been added. Only one oil-immersed vacuum pump is used as an auxiliary. This is connected to the line terminating in stopcock S_4.

The technique of operation is merely a simplified version of the operation of the complete unit, which is fully described in the following section on procedures.

(*c*) The Experimental Unit.—A photograph of the experimental unit (fig. 13) and the distillation train of this apparatus (fig. 14) are reproduced. This assembly included other types of distillation tubes, adsorption tubes, vapor-pressure manometers, etc., which are not described in the present paper.

These photographs illustrate the type of mounting recommended. The basic mounting is an iron frame constructed from ½-inch steel rods spaced 4 inches apart and firmly anchored with angle braces at the back and flanges at the bottom. Ordinary V type clamp holders are used to secure the apparatus supports. These supports consist of cups cast in graduated sizes, into which bulbs and heavier parts are set in plaster of Paris. Tubes are secured with small clamps also cast in graduated sizes. The glass tube is wrapped with ordinary ½-inch adhesive tape before the clamp is applied. Such clamps occupy little space.

This type of mounting has three distinct advantages. When properly assembled, no strains are left in the glass connections, and expansion joints are unnecessary; a wooden support is likely to warp

and so develop strains in fused glass joints. The whole apparatus is easily accessible to the glass-blower's torch. When a wooden mounting is used this is not invariably the case, and even when openings are provided in a wooden backing a distressing amount of destructive distillation of wood is apt to occur when repairs to the glass parts become necessary. The apparatus can be easily and quickly changed to suit experimental developments or special needs. If other advantages were lacking, this one alone would justify the use of the mounting here described.

V. GENERAL PROCEDURES

When general procedures are explained, direct reference will be made to the assembly diagram. (Fig. 10.) As previously noted, corresponding parts of other line drawings and photographs have been identically lettered.

1. PREPARATION OF APPARATUS FOR A DETERMINATION

To prepare the apparatus for a determination, the mercury and gas reservoirs (R series), burettes (B series), and capillary distributor train (stopcocks *5* to *17*) are filled with clean mercury.

The entire distillation train (*I* to *V*), condensation bulbs (C series), connections to pressure gauges (M series), and traps T_1 and T_2 are evacuated by opening all interconnecting stopcocks and using the mercury vapor pump (V_1) with a mechanical backing pump (vacuum No. 2). During this operation stopcocks *18* and *19* are opened and stopcock *20* is closed. The very small residual pressure left by the mechanical pump in the line between the mercury vapor pump nozzle and stopcocks *18* and *20* may be removed if necessary by closing stopcocks *18* and *19* and opening stopcock *20*, which allows the Töpler pump (V_2) to back the mercury vapor pump. Stopcocks *18* and *19* remain closed during a subsequent determination.

The McLeod gauge (M_2) is used to measure the degree of evacuation. When this indicates a pressure of 0.0001 mm Hg or less, and the apparatus has been pumped sufficiently long to remove water vapor and gases adhering to the glass walls,[16] the unit should be closed to the pump and allowed to stand overnight in order to detect possible leaks. Tube *II* should be immersed in liquid air. If the pressure increase during this interval is no greater than 0.0005 mm, the apparatus may be considered to be in a satisfactory state for the present work, although it is to be preferred that the McLeod gauge indicates no increase of pressure. Leaks may be isolated and detected by closing all interconnecting stopcocks, opening them one at a time, and noting in which section pressure has built up. A high-frequency discharge may then be used to locate the actual point of leakage.

[16] This may require as long as 24 hours continuous pumping when the glass parts have not been heated previously.

2. ORDER OF PROCEDURE DURING A SINGLE DETERMINATION

The course taken by a gas sample and the various manipulations to which it is subjected during a single determination may be traced with reference to the assembly diagram. (Fig. 10.) After this is understood the various manipulations may be described in detail.

The sample is introduced at stopcock *11*, measured in the burette B_2 and transferred through the capillary distributor train through stopcock *5* to the mercury trap M_1 and thence through stopcock *40* to the distillation train (*II*). Here it is separated into three fractions by a system of isothermal fractional distillation at low temperatures. The first fraction consists of isobutane plus lower boiling components and is transferred by pumping and condensation from the distillation train through the pumps V_1 and V_2 and bulb C_6, and by direct condensation to bulb C_1, to the burette B_2, where its volume is determined. It is then stored in the reservoir R_7. The second fraction consists of normal butane, which is removed from the distillation train by direct condensation in the bulb C_1, and thence vaporized into the burette B_2 and there measured and retained. The third fraction consists of pentane and higher boiling hydrocarbons. Throughout this paper frequent reference will be made to this fraction, which, for the sake of brevity, will be called simply the "pentane fraction." Its liquid volume is determined in the burette B_1. It is then transferred by condensation to the bulb C_2 and its vapor pressure determined at a chosen fixed temperature. Measured increments of the butane fraction are condensed from the burette B_2 into the mixture contained in the bulb C_2, and the increase of vapor pressure observed for each increment of butane. The mixture of butane with the pentane fraction may also be measured in the liquid phase with each addition of butane. This completes the operation for a single determination.

3. MEASUREMENT OF GAS VOLUMES

The gas burette is connected to the distribution train to permit the sweeping out of a sampling line through stopcocks *11*, *10*, *27*, and *26* in series. The side arm leading from the sampling outlet of stopcock *11* is immersed in mercury and acts as a manometer to indicate proper adjustment of pressure during the transfer of the sample. This is quite convenient if the sample is taken from a cylinder under pressure. Mercury is drawn into the burette reservoir R_3 by vacuum (No. 3) and flows back under atmospheric pressure.

A sample of 1 to 2 liters should be taken. The bulbed burette recommended is capable of determining the volume of the whole or any fraction by a single measurement and saves considerable time over an instrument of smaller capacity. The fractions and the original sample are measured against the same compensator pressure

and for convenience are usually measured saturated with water vapor. Since the distilled fractions emerge quite dry, care must be taken to insure their saturation in the burette.

It is necessary to calibrate the condensation bulb C_1 so that its volume and that of the connections from stopcock *28* to stopcock *25* are known. This volume is then added to the burette reading when gas has been transferred for measurement through the medium of condensation in C_1 and subsequent vaporization into B_2.

Reference to the detailed operation of the burette of Figure 1 has already been made.[17] An ordinary gas analysis burette may be used, but is not as satisfactory with respect to accuracy, speed, and convenience.

4. TRANSFER OF GAS VOLUMES

The initial evacuation of the apparatus has been described. Subsequent transfer of gas volumes is done by the pumps V_1 and V_2 acting in series and by the method of alternate condensations and vaporizations.

The first fraction resulting from the distillation is transferred by both of the above methods. The nitrogen and a portion of the methane are pumped from the distillation train through stopcocks *1* and *2*, adjusted to by-pass the P_2O_5 drier, and thence through the mercury vapor and Töpler pumps to the reservoir *12*. This gas is then transferred by mercury displacement to reservoir *11* and thence to the burette B_2. During this pumping the major portion of the methane pumped by V_1 has been collected in the bulb C_6 by condensation at $-210°$ C. Since its vapor pressure is less than 1 mm of mercury at this temperature, the mass of the vapor over the solid is very small. Stopcocks *20* and *22* are closed, and the methane condensate is vaporized through stopcocks *21*, *23*, *16–10*, and *27* into the burette. The residual gas in the bulb C_6 is removed by the Töpler pump and transferred to the burette. The greater portion of the methane in the original sample is condensed in tube V at $-210°$ C., and this, together with the ethane, propane, and isobutane which are separated in a following step, is removed from tube V by vaporization therein and condensation at liquid air temperatures in the bulb C_1. This condensate is in turn vaporized into the burette, and the total volume of the isobutane and lower boiling components is determined at one measurement. It is then transferred by mercury displacement to the reservoir R_7, stopcock *3* being opened to the atmosphere and stopcock *4* to vacuum No. 3 for this purpose.

The other fractions are transferred directly by condensation at liquid air temperatures to the desired bulbs. Bulbs C_3, C_4, and C_5, may be used for the storage of fractions in the liquid phase.

[17] See footnote 6, p. 1151.

Since methane possesses a vapor pressure of approximately only 1 mm Hg at −210° C., and the vapor pressures of ethane or higher boiling components are negligible at ordinary liquid air temperatures, the presence of nitrogen alone makes necessary the complication of a mercury pump. As it is, a great deal of time is saved by using the mercury pump to remove the nitrogen only.

5. OPERATION OF THE DISTILLATION TRAIN

The gas sample enters the evacuated distillation train through the mercury trap T_1. This is designed to permit the draining of the entrapped mercury while the distillation train is under reduced pressure, an operation performed by opening stopcock *37* to vacuum line No. 3, draining through stopcock *38*, and subsequently draining through stopcock *39* with stopcock *38* closed and stopcock *37* turned to the atmosphere.

The pressures within the distillation train are read by the barometric manometers M_1, M_3, M_4, and M_5 and the McLeod gauge M_2. The latter compression manometer is connected to the train through a 120° stopcock (*42*), which permits the reading of pressures in tubes *II* and *III* independently. A second gauge so connected to tubes *IV* and *V* is very helpful during more involved separations.

Stopcocks *43*, *45*, *47*, and *49*, with outlets leading through ordinary rubber stoppers, may be connected to either air or vacuum line No. 1. This vacuum provides a means of boiling liquid air under reduced pressure. The mouth of the Dewar tube containing the liquid air may be made to seat satisfactorily around the rubber stopper when vacuum is applied, if care is taken to dry the tapered sides of the stopper. This simple device works quite as well as the ordinarily used large rubber tube surrounding the outside of both stopper and Dewar tube, since the applied vacuum strongly seats the stopper.

When the sample is first transferred from the burette, stopcocks *31*, *40*, *41*, *42*, *44*, *46*, *48*, *50*, *51*, *52*, *57*, *28*, *1*, *18*, *19*, and *21* should all be closed. Tubes *II*, *III*, and *IV* are surrounded with liquid air and tube *V* and bulb C_6 with liquid air boiling under reduced pressure (approximately 20 mm).

Stopcock *40* is opened to slowly admit the sample to tube *II*. The condensation which takes place should not be too rapid and may be gauged by the boiling of the liquid air surrounding this tube. If the sample contains little nitrogen, it will be possible to transfer all of it into tube *II*. If the partial pressure of the nitrogen is sufficiently high, the pressure will build up to exceed atmospheric. When this condition is indicated by the barometric manometer M_1, stopcock *40* is closed and stopcock *44* carefully opened until the manometers M_1 and M_3 indicate equal pressures. Stopcock *44* is then closed and *40* again opened, the operation being repeated, and possibly extended

to tubes *IV* and *V*, until the total sample has been transferred from the burette and followed by a displacing column of mercury through the distribution train and into the trap T_1.

When the sample has been completely transferred, its actual separation is started. The detailed description of this process will follow. (Sec. VI.) The general operating procedure is given in the following paragraphs.

The method of separation depends upon the presence of condensable gases only, since the courses of all distillations are followed directly by observing relevant vapor pressures, and the distillates themselves are transferred entirely by condensation. The first step of the separation is therefore the removal of nitrogen, which does not condense at the lowest temperature employed. This is accomplished by pumping from the distillation tubes as described in Section VI.

When the nitrogen is removed, the hydrocarbons are separated by a system of isothermal distillation. The fraction to be separated is held at a constant temperature in one of the distilling tubes, or, if the rectifying tube (*I*) is used, a uniform temperature gradient is held over the length of the column. The distilling temperature is determined from a study of the vapor pressures of the pure components and should be chosen so that the component to be distilled possesses an appreciable vapor pressure while the component of next higher boiling point has a practically negligible vapor pressure. With the distilling tube held at such a temperature, the next tube in the series is surrounded with a bath, the temperature of which is sufficiently low to lower to a negligible figure the vapor pressure of the component to be distilled over. When the two tubes are then connected through the intermediate stopcock, the low boiling component vaporizes at the higher distilling temperature and liquefies at the lower condensing temperature. The operation required in a single distillation is then simply the adjustment of these two temperatures and the turning of a stopcock.

Since, in the course of a single distillation, some of a higher boiling component may distill over with the low boiling one, the distillate is partially vaporized and recondensed at the temperature selected for the next distillation. A second distillation is then made, the distillate being collected as before by condensation in the next tube in the series and the residue transferred back to the first tube. In this manner the distillates move progressively forward and the residues backward with each distillation. The system then requires a minimum of three distilling tubes, but as many more may be added as the operator wishes. The additional tubes permit conducting two or more separate distillations at one time, which is a great time saver. Five is probably as many as will be convenient in most cases.

The course of a single distillation is followed entirely by observing the vapor pressures. A tube is adjusted to the proper temperature for a distillation, and the vapor pressure of the contained mixture is observed. When the distilling tube is connected to the condensing tube, this pressure drops to some intermediate value and from this gradually diminishes to become equal to or less than the saturation pressure of the low boiling component in its pure state, measured at the condensing temperature. This provides a first basis for judging the completion of a distillation.

If, during the course of a distillation, the stopcock is closed between the distilling and condensing tubes, the pressure in the distilling tube will gradually approach the originally observed vapor pressure if the low-boiling component is present. On the other hand, it will not change if this component has been removed. This provides a second basis for determining the completion of the distillation.

If the distilling tube then remains shut off from the condensing tube and the residue contained in the distilling tube is totally or partially vaporized at room temperature and subsequently cooled to the same distilling temperature as before, an increase over the vapor pressure observed just before this vaporization indicates the presence of further traces of the low-boiling component.

If the distillate from a first distillation is redistilled, the resulting third distillate may have a higher vapor pressure than the previously observed pressure of the second distillate, measured at the same distilling temperature, and so indicate the presence of a higher-boiling component in the second distillate. A further comparison of the saturation pressures of this third and a fourth distillate, and so on, until they become equal, will finally establish the fact that the higher-boiling component has been removed.

If a fraction be distilled so that a small initial distillate and a small final residue may be condensed at an identical temperature (surrounded by the same well-stirred bath) and their vapor pressures measured simultaneously, either by two of the manometers of the apparatus or by a differential manometer, the purity of the fraction so tested may be established or disproved. This test is quite severe. It will be discussed in detail in part 7 of this section. From such simple vapor-pressure observations as these, the proper course of a distillation may be determined and its progress followed.

In performing a separation it is unnecessary to determine accurately the vapor volumes of each distillate and residue; but the vapor volumes of the residues and distillates obtained toward the end of the separation of any component indicate the completeness of this separation. The volumes are usually very small, and their relative order of magnitude may be determined by simply reading the pressures on various barometric manometers when the distilling tubes are at room

temperature. These small final volumes form a still further means of determining the progress of a distillation, but they alone are very misleading, since it is possible to collect a distillate almost indefinitely, though very slowly, long after the desired component is removed. A new operator has a tendency to do this very thing and therefore should give careful consideration to the discussion of vapor pressure observations.

The vapor pressures of the hydrocarbons at very low temperatures are not accurately known, although their orders of magnitude are well established and reasonably good approximations can be computed. These data would be quite helpful in following the course of a distillation, but they are not entirely necessary and serve only as rough guides. This is obviously true when the lowering of vapor pressure by higher boiling impurities is considered. It would not be logical—for example, in distilling propane from a mixture of butane and pentane—to consider the propane removed from the higher boiling components when the vapor pressure of the residue had been lowered to that of butane at the particular distilling temperature employed. It would be necessary to continue the distillation until the vapor pressure of the residue is somewhat lower. For this reason the exact adjustment of distillation temperature is not important, except when comparative vapor pressure readings are to be taken.

From a consideration of the foregoing paragraph it is apparent that a distillation is more readily followed if only two components are present. This should usually be approached as nearly as possible in actual practice. For example, if propane is to be separated from butane and heavier hydrocarbons, it may be of advantage to make an initial cut which will include all of the propane with a great deal of butane and possible traces of pentane and proceed to separate the propane from this mixture rather than from the total residue. The decision as to the worth of this step is made entirely on the basis of the composition of the original gas. If the partial pressures of propane and higher boiling components are apparently relatively high, the step will save time.

6. MEASUREMENT OF VAPOR PRESSURES

A true equilibrium between liquid and vapor phases is somewhat difficult to achieve and maintain. Since the rapid attainment of true equilibrium requires stirring, the vapor pressures measured in the distilling tubes are not likely to be quite correct; but because of the small volumes used and the relatively large surface of liquid exposed they should be very near the correct values. Care must be taken to see that some condensate is present, so that a saturation pressure and not a fixed gas pressure is measured. The precaution is mentioned since the case often obtains where very small volumes of liquid exist. If the pressure is low within the distillation tube, it is necessary to

allow 10 to 12 minutes for proper adjustment of temperature equilibrium between the copper block and the interior of the distillation tube.

When the manometer M_6 is used, the condensate may be very simply stirred by vibrating the long, thin stem of the bulb C_2. This method may appear crude; yet it not only produces very satisfactory mixing, but it is the only practical means because of the very small liquid volumes resulting from a 1-liter sample. An electro-magnetic stirring device within the bulb is impractical in this instance.

The arm of the manometer M_6 adjacent to the condensing bulb should be maintained at the same temperature as the bulb itself if vapor pressures of pentane and heavier hydrocarbons are to be measured above room temperature. If this is not done, distillation from the bulb and condensation in the manometer arm will occur, with resultant error in the observed saturation pressure.

When the manometer M_6 is used for the measurement of the vapor pressures of the pentane fraction and mixtures of this fraction with butane, a special precaution is necessary. The relevant pressure to be observed in this instance is the vapor pressure of the mixture when the liquid phase is in equilibrium with an infinitesimal amount of the vapor phase. The maximum vapor pressure (for the given mixture at any fixed temperature) is thus attained. It is possible to obtain this pressure by extrapolation of pressure measurements made at various volume ratios of liquid and vapor phase, but it is not necessary to go to this extent in the present work. The required theoretical equilibrium is nearly obtained in practice by reducing the volume of the vapor phase by means of capillary connections between the bulb containing the liquid and the manometer and by measuring the pressure with the mercury meniscus adjacent to the condensing bulb at an etch mark placed at the top of the manometer arm. The manometer arms should be constructed of matched tubing of capillary bore (2 mm). The bulb should be nearly filled with condensate. Under such conditions the volume of the vapor phase is practically negligible as compared with the total volume of the material in the vapor phase.

7. DETERMINATION OF PURITIES OF THE DISTILLATES

The manometer M_6 may be used for determining the purity of a fraction by a partial isothermal condensation. This is the method ordinarily employed as a criterion of purity, and references to it may be found in the work of Onnes and others. Equations for the quantitative determination of impurities present in a nearly pure substance, depending upon behavior during an isothermal condensation or vaporization, have recently been computed by E. W. Washburn.[18]

[18] E. W. Washburn, Zeit. Phys. Chem. (Cohen-Festband), p. 592; 1927.

The differential manometer provides a somewhat simpler method for testing the purity of a distillate. This eliminates the necessity of a carefully controlled temperature during the progress of an isothermal condensation and at the same time is a more severe criterion of purity. The manometer previously described (Sec. IV, 7 and fig. 8) is used. A distillate whose purity is to be tested is separated by a final distillation into (1) a small initial distillate which is condensed in B_2 of the manometer, (2) a large middle fraction which is condensed for storage in bulb C_3 of the train, and (3) a small final residue which is condensed in B_1 of the manometer. The vapor pressures of the initial distillate and final residue are then directly compared, B_1 and B_2 being immersed in the same bath. To insure uniformity of temperature within B_1 and B_2, mercury is frozen about them. The temperature selected should be such that the pure substance in question will have an appreciable vapor pressure (5 to 15 mm of mercury).

If a quantitative estimate of purity is desired, the vapor pressure of a small initial distillate should be compared with that of the entire remaining fraction, and the equations of Washburn [19] applied. It is evident that in extended work of this nature it would be desirable to prepare a set of manometers each containing one of the hydrocarbons carefully purified. The purity of any distillate could be determined quickly by the use of such a reference set.

VI. SEPARATION OF GAS SAMPLE BY FRACTIONAL DISTILLATION

1. ISOBUTANE, PROPANE, AND LOWER BOILING COMPONENTS

This fraction consists of nitrogen, methane, ethane, propane, and isobutane, together with traces of oxygen, carbon dioxide, the rare gases, and the lower boiling unsaturated compounds, if present. Oxygen, together with any rare gases, is separated with the nitrogen; and carbon dioxide, ethylene, propylene, and some of the butylene, if present, are included in the same fraction as the distillation proceeds. Oxygen and carbon dioxide usually occur in traces, although some natural gases contain appreciable amounts of the latter, in which case it should be removed by absorption in sodium or potassium hydroxide before the distillation. The unsaturated compounds are usually not present, and isobutane occurs only in relatively small amounts.

As previously shown, the nitrogen should be removed before the distillation proper is begun. This step would be simple enough were it not for the appreciable solubility of nitrogen in the hydrocarbons at low temperatures. It has not been found feasible to begin this step directly at a temperature suitable for the separation of propane

[19] See footnote 18, p. 1169.

from butane because of the danger of carrying over the higher boiling components. Hence, tubes *II*, *III*, and *IV* are maintained at liquid air temperatures and tube *V* at −210° C. The sample is transferred to the distillation train, and stopcock *1* is then slowly opened to connect the distilling train to the mercury vapor pump, condensation bulb C_6 at −210° C., and the Töpler pump in series. When the pressure indicated by the manometer M_4 has been lowered to approximately 1 mm, stopcocks *48*, *46*, and *44* are closed, the pump remaining connected to tube *V*. This step accomplishes the removal of the bulk of the nitrogen.

It is now necessary to remove traces of nitrogen left in solution, and at the same time desirable to distill off the methane and the major portion of the ethane. The residue left will then consist principally of propane and heavier components, and the separation of propane and isobutane may be more easily followed without the confusion of the comparatively high vapor pressure readings of ethane and methane at the higher temperatures employed for the propane separation. This step is accomplished as follows: The liquid air bath is removed from tube *II* and the residue therein allowed to vaporize until the manometer M_1 registers slightly under atmospheric pressure. A copper temperature control block previously cooled to approximately −160° C. is quickly placed around *II*, and time allowed for proper adjustment of temperature equilibrium. The stopcocks *44*, *46*, and *48* are again slowly opened in order. When the pressure in the distillation train has dropped to 1 mm, the nitrogen has usually been completely removed from the residue in *II*, but traces of nitrogen may still remain in solution in the condensate in *V*. This condensate will contain methane and ethane, with possibly some traces of propane, depending on the composition of the original sample. Stopcocks *4*, *8*, and *1* are closed, and this fraction is vaporized from *V* and condensed in C_1 for transference to the burette. Stopcock *29* is then closed and stopcock *1* opened to pump the residual vapor from *V*. When M_5 indicates no pressure, stopcock *1* is again closed, and the condensate in C_6 vaporized to the burette as described in Section V, 4.

The residue in *II* will contain traces of ethane and rarely methane, together with the major portion of the propane and all isobutane and higher boiling components. The separation of this fraction is usually best done by making an initial distillation at a higher temperature than would be used normally. This will result in distilling over some normal butane or even traces of pentane but leaves a residue free from propane and isobutane. In the case of a "dry" gas (one containing small amounts of the higher boiling hydrocarbons), the separation may be made in tubes *II*–*V*, but time is ordinarily saved by using the rectifying tube *I*. One distillation made in tube *I* has accomplished the same degree of separation as 6 to 10 made in the ordinary tubes.

In the case of "wet" gases (containing large amounts of higher boiling hydrocarbons), this is particularly noticed.

The residue in *II* is accordingly transferred to the distilling tube *I*. The temperature gradient of *I* is adjusted to the range −80° C. at the bottom to −110° C. at the top, and *I* is then opened through *II* to *III*, the latter tube being cooled to liquid air temperature. If the original sample contains relatively high partial pressures of propane and higher boiling components, it may be necessary to cool *III* to −210° C. to condense possible traces of methane which has been held in solution, although this step is usually unnecessary. The distillation from *I* to *III* is allowed to proceed until the McLeod gauge M_2 indicates a pressure of approximately 0.3 mm with stopcock *44* closed and *42* opened to *II*. The distillate in *III* is then vaporized and recondensed at −120° C. A distillation of this mixture is now made, the resulting distillate being collected in *IV* by condensation at liquid air temperature. This distillation is halted when the McLeod gauge, now connected through stopcock *42* to *III*, registers a pressure of 0.2 to 0.3 mm with stopcock *46* closed (that is, the vapor pressure of the residue is measured). This residue may still contain isobutane and traces of propane, and the new distillate may contain some butane. Accordingly, a further distillation is made from *IV* at −120° C. to *V* at liquid air temperature, and the residue from this is transferred to *III*, where the combined residues are again distilled at −120° C. to continue the separation of isobutane and possible traces of propane. This procedure is continued until the final distillates show no further increase in vapor pressure and the vapor pressures of the final residues indicate no isobutane present. It should be noted that while no great harm will result in carrying over some butane with the final fraction, no isobutane or traces of propane must be left in the residue, since these components would later cause considerable error if included in the normal butane fraction.

It is impossible to state how many such distillations will be required to complete the separation. A "dry" gas will naturally require fewer than a "wet" gas. The fractionation charts which follow illustrate typical examples. The operator should not make the mistake of following these charts step by step, since every natural gas is a separate problem and may require more or less fractionation than the charts illustrate. The charts given are merely examples showing the general trend of such separations.

When the separation of the propane fraction has been completed, the vapor volume of the distillate is determined, after which it may be stored for further check in the reservoirs R_{7-9}, or discarded.

2. BUTANE FRACTION

The final residue from the above distillation is transferred to distilling tube *I*, and an initial separation is made with a temperature gradient of −60 to −90° C. over the column. The distillate, which is collected at liquid air temperature in tube *III*, will contain practically all of the normal butane and some pentane. It is accordingly distilled from *III* at a temperature of −100° C. into *IV* at liquid air temperature and the residue returned to *I*, where a second separation is made with a temperature gradient of −70° to −100°. This distillate is collected in *III* and again separated at −100°, the new distillate being combined with the former contained in *IV*. A distillation from *IV* to *V* may result in further separation, in which case the residue is returned to *II*. The residue in *I* is combined with this, and a distillation from *II* to *III* is carefully conducted to ascertain if traces of butane still remain in the pentane fraction. If butane is detected in this distillate, a double distillation from *III* to *IV* and *IV* to *V* is necessary to free it from pentane carried over with the initial distillation from *II* to *III*. In the case of a gas containing a large proportion of butane and heavier hydrocarbons—as, for example, accumulator condensates, higher boiling fractions from stills or rectifying columns, etc.—the separation is tedious. If the operator has to deal with a large number of such samples, a series of distilling tubes of the rectifying type (tube *I*) are recommended.

3. PENTANE AND HIGHER BOILING COMPONENTS

This fraction remains as a residue from the previous separations and for the present purpose need not be further separated, since all of its components fall naturally into the classification "natural gasoline." If the separation of this residue is desired for any especial reason, it is best done in a rectifying column similar to that shown in Figure 6. For consistent analytical results a much longer column and a large volume of such a residue are essential. A small rectifying column equipped with bubbling cap plates and reflux drains is to be preferred. Such separations are out of the scope of the present work.

4. FRACTIONATION CHARTS

(*a*) Types of Gases Separated.—The fractionation charts (figs. 15 to 21) which follow illustrate the steps necessary for the separation of several types of natural gases. The separations have been carried out in more detail than will generally be necessary for a determination of natural gasoline, but this detail will serve to instruct the beginner who may have difficulty in determining the proper end points of the individual fractionations, as well as the actual plans of attack. Separations carried to the extent of those indicated on the fraction-

ation charts usually result in analyses checking within 0.01 to 0.02 per cent, an accuracy slightly higher than that usually required for a determination of natural gasoline.

Fractionation chart No. 1 illustrates the separation of a natural gas containing 91.79 per cent $N_2+CH_4+C_2H_6$, 5.97 per cent C_3H_8, 1.45 per cent C_4H_{10}, and 0.79 per cent $C_5H_{12}+$ higher boiling C_nH_{2n+2}. The sample was taken at an Oklahoma extraction plant.

Fractionation chart No. 2 illustrates the separation of a Pennsylvania natural gas taken at the inlet of a natural gasoline adsorption plant. Chart No. 3 shows the separation of this same gas by use of the rectifying type distillation tube, while chart No. 4 illustrates the separation of the outlet gas from the same plant. The composition of the inlet gas was 96.22 per cent $N_2+CH_4+C_2H_6+C_3H_8$, 2.28 per cent C_4H_{10} and 1.50 per cent $C_5H_{12}+$higher boiling C_nH_{2n+2}, while the outlet gas contained 97.9 per cent $N_2+CH_4+C_2H_6+C_3H_8$, 1.85 per cent C_4H_{10}, and 0.15 per cent $C_5H_{12}+$higher boiling C_nH_{2n+2}.

Fractionation chart No. 5 illustrates the separation of a Wyoming natural gas containing large amounts of the heavier hydrocarbons: 74.20 per cent $N_2+CH_4+C_2H_6$, 19.20 per cent C_3H_8, 4.41 per cent C_4H_{10}, and 3.19 per cent $C_5H_{12}+$higher boiling C_nH_{2n+2}. The fractionation of this gas is quite different from that of the "drier" gases preceding.

Chart No. 6 shows the separation of a commercial propane and illustrates in a general way what can be done with special still samples.

Chart No. 7 illustrates the separation of the nitrogen-methane fraction and the ethane fraction from a "wet" natural gas and is included for reference by those who wish to determine the entire composition of a natural gas as well as its natural gasoline content.

(*b*) KEY TO INTERPRETATION OF FRACTIONATION CHARTS.—The various steps of the fractionation have been abbreviated on the charts because of the small space allowed for presentation.

The Roman numerals represent the distilling tubes as they occur on the assembly diagram. (Fig. 10.)

The data expressed to the right of each Roman numeral are arranged in the following order:

1. Kind of procedure.
2. Temperature in $-°C$.
3. Pressure in mm Hg.

The kind of procedure is abbreviated thus:

c, indicates a condensation.

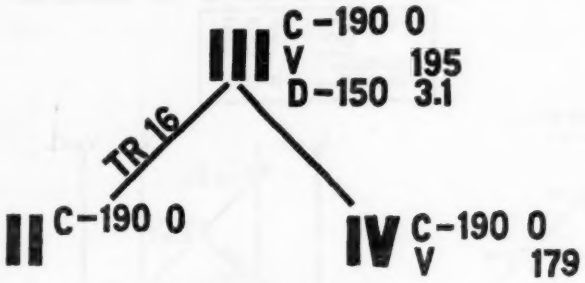
v, indicates a vaporization.

d, indicates a distillation.

tr, indicates a transfer without distillation.

When the directional lines of a chart lead to the symbols $V_1V_2C_6$, the gas has been pumped by the mercury vapor pump (V_1) and

automatic Töpler pump (V_2) and condensed in the bulb (C_6), from which it is transferred to the burette (B_2) for measurement. An example may be taken to illustrate.



Key to fractionation charts

The interpretation is as follows: A mixture in tube *III* has been condensed at −190° C. to a pressure of 0 mm. It has then been vaporized at an unmeasured temperature (always that of the room) with the resulting gas pressure (not vapor pressure) of 195 mm. It was then distilled at −150° C., at which temperature it possessed an initial vapor pressure of 3.1 mm. The distillate was collected in *IV* at −190° C., where it was condensed to a pressure 0 mm. This distillate was vaporized at unmeasured (room) temperature to a pressure of 179 mm. The residue left in *III* was vaporized and transferred to *II*, where it was condensed at −190° C. to 0 mm. Its vaporized pressure was 16 mm.

NOTE.—The relation 195 mm (pressure of original mixture when vaporized) −179 mm (pressure of vaporized distillate) =16 mm (pressure of vaporized residue) will, of course, not hold accurately in the actual apparatus, since the vapor spaces in these tubes are not all identical, and atmospheric temperature does not remain constant.

(*c*) DISCUSSION OF CHARTS.—*Fractionation chart No. 1* (*fig. 15*).—Since the percentage of propane was desired in addition to the natural gasoline content, the analysis was made to include this extra determination. Nitrogen, methane, and ethane were grouped for the first fraction. The first step consisted in merely drawing off the nitrogen, together with most of the methane and some ethane. This was accomplished by pumping from bulbs *I* to *IV* in series, all held at −185° C. The residues were then transferred back to *I*, and the separation of the remaining ethane from the propane and higher boiling constituents was carried out by a series of distillations at −150° C.

It will be noted that the initial vapor pressure of this series was 18 mm at −150°, which clearly indicated the incomplete removal of methane at this point. Since the separation may be best followed with reference to the vapor pressures of ethane and propane alone,

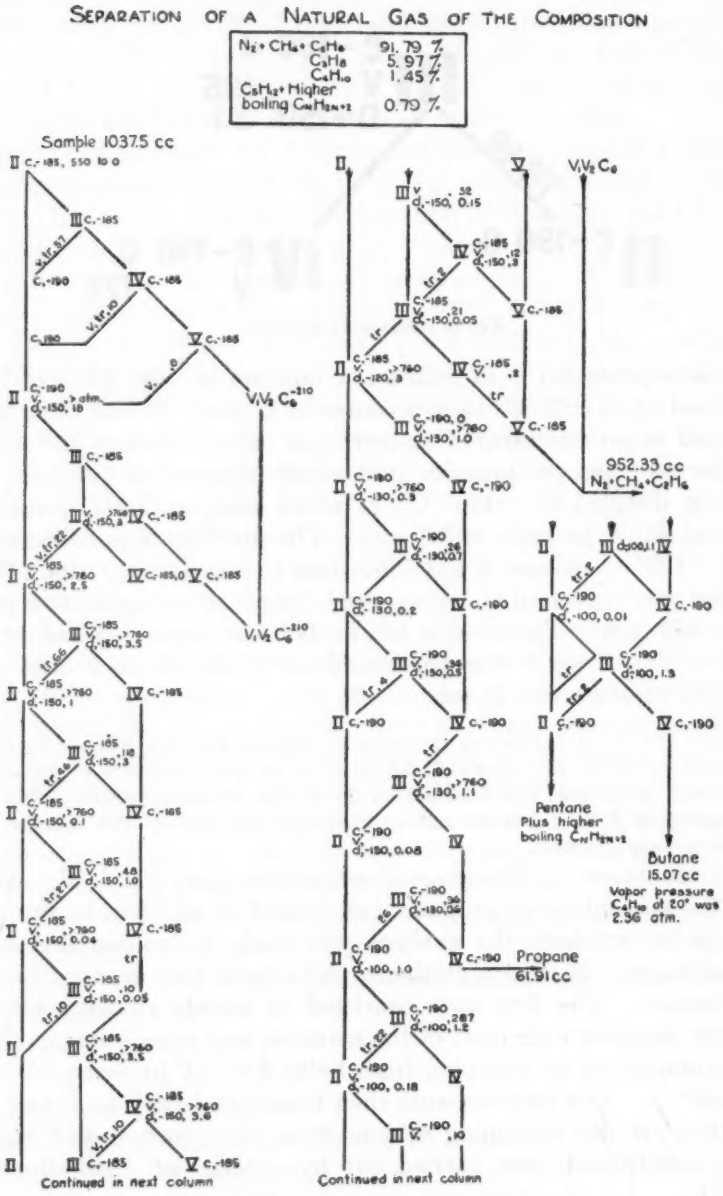

SEPARATION OF A NATURAL GAS OF THE COMPOSITION
N₂+CH₄+C₂H₆ 91.79 %
C₃H₈ 5.97 %
C₄H₁₀ 1.45 %
C₅H₁₂+Higher boiling CₙH₂ₙ₊₂ 0.79 %
Sample 1037.5 cc
952.33 cc N₂+CH₄+C₂H₆
Pentane Plus higher boiling CₙH₂ₙ₊₂
Butane 15.07 cc
Vapor pressure C₄H₁₀ at 20° was 2.36 atm.
Propane 61.91 cc
Continued in next column
Continued in next column

FIGURE 15.—*Fractionation chart No. 1*

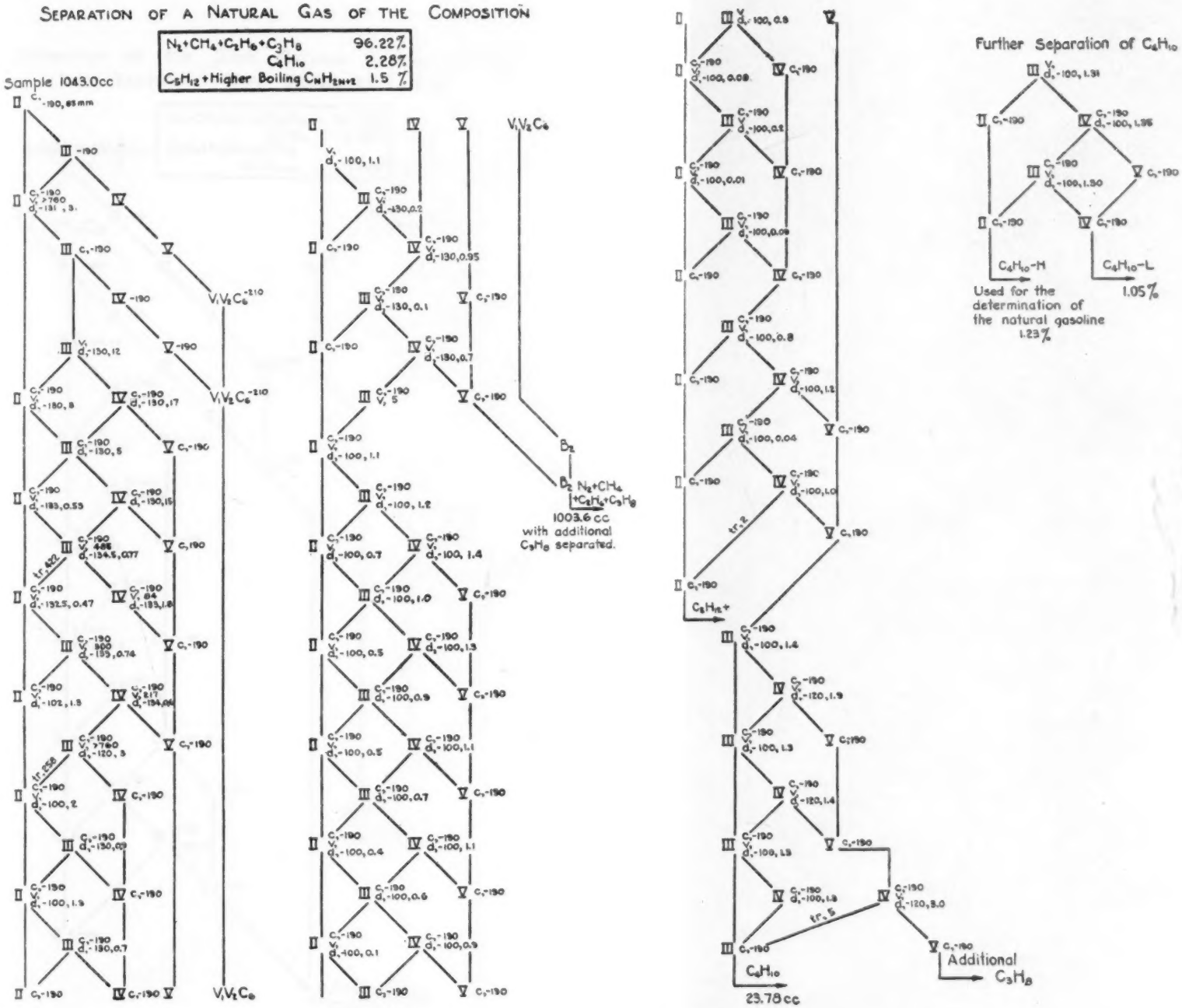


FIGURE 16.—*Fractionation chart No. 2*

47559°—29. (Face p. 1176.)

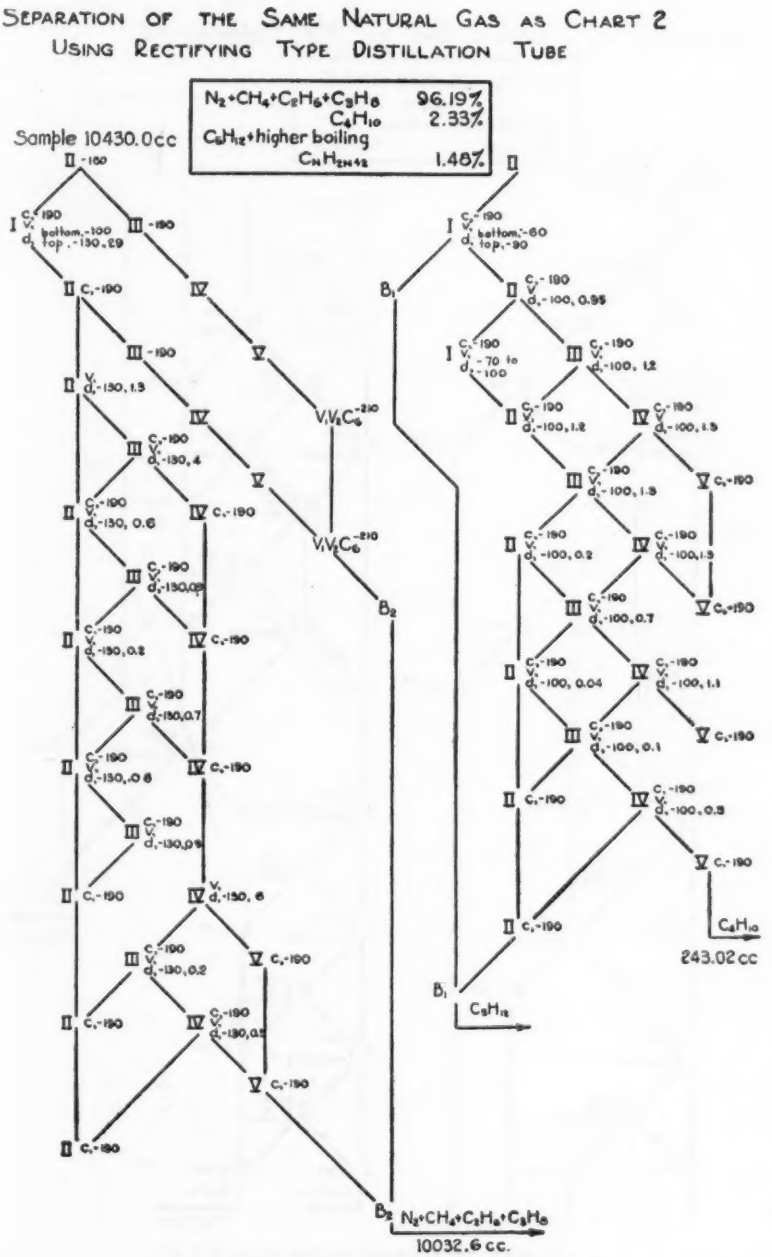


FIGURE 17.—*Fractionation chart No. 3*

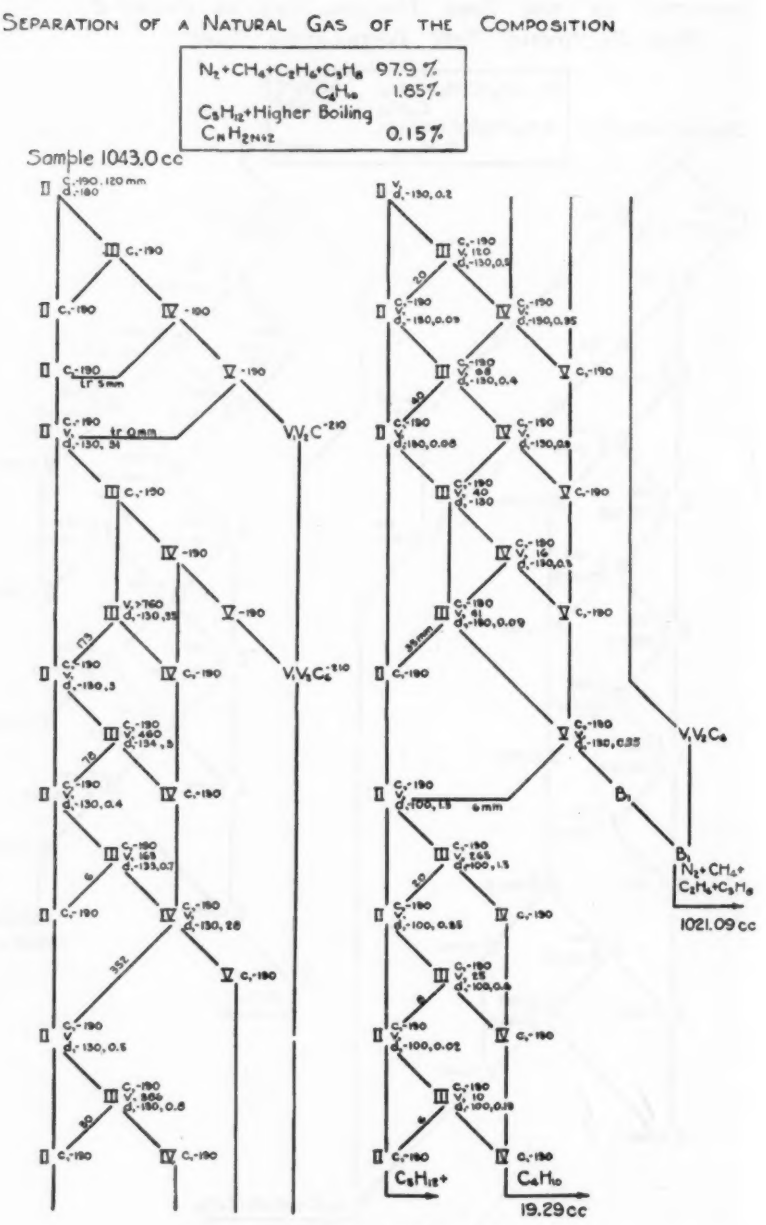


FIGURE 18.—*Fractionation chart No. 4*

SEPARATION OF A GAS OF THE COMPOSITION

$N_2+CH_4+C_2H_6$	74.20%
C_3H_8	19.20
C_4H_{10}	4.41
C_5H_{12}+Higher Boiling C_nH_{2n+2}	3.19

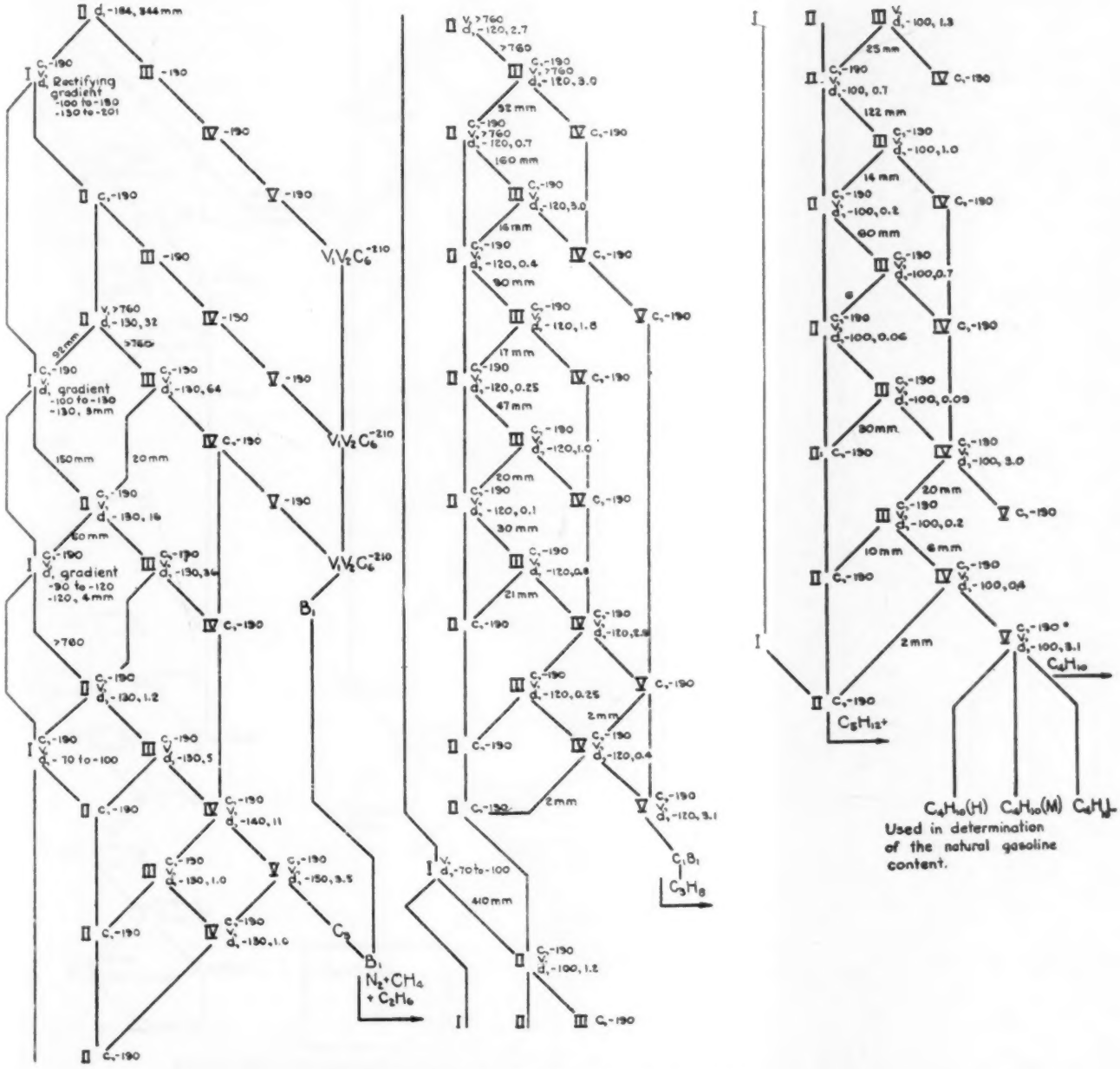


FIGURE 19.—*Fractionation chart No. 5*

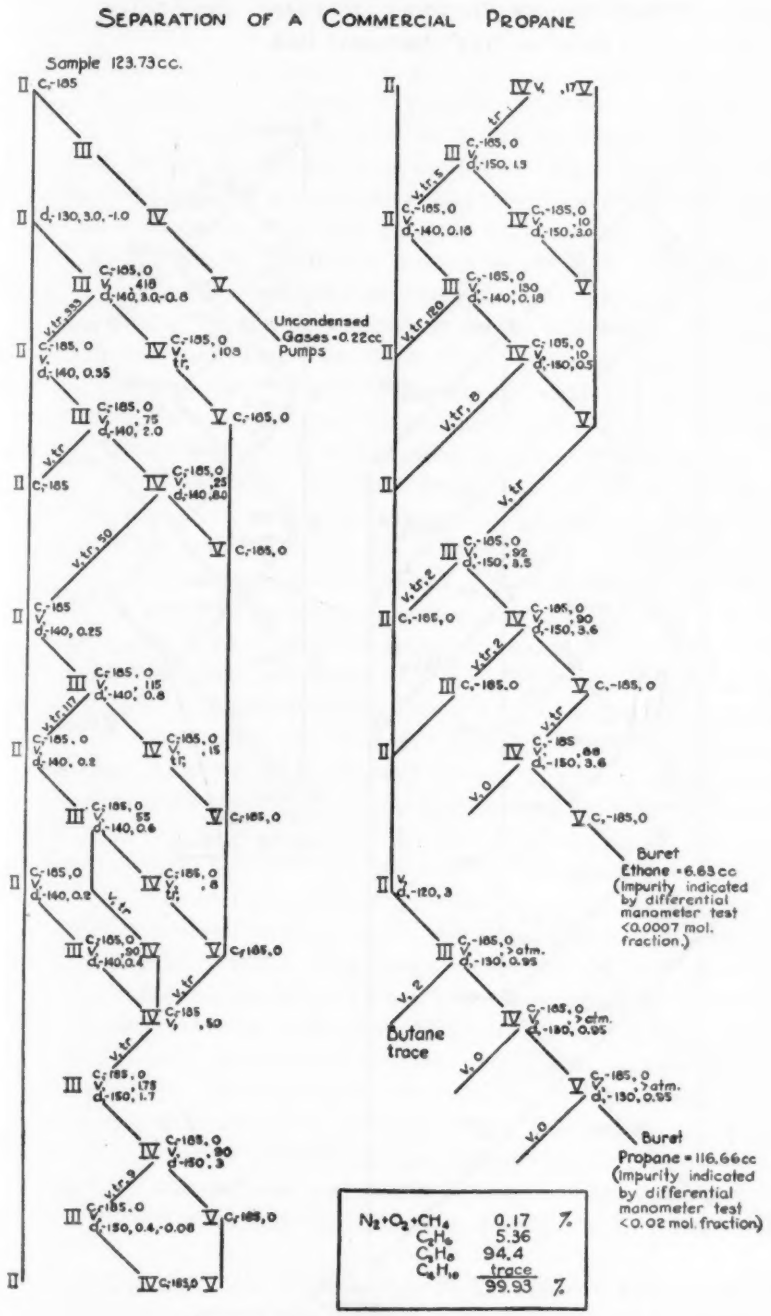


FIGURE 20.—*Fractionation chart No. 6*

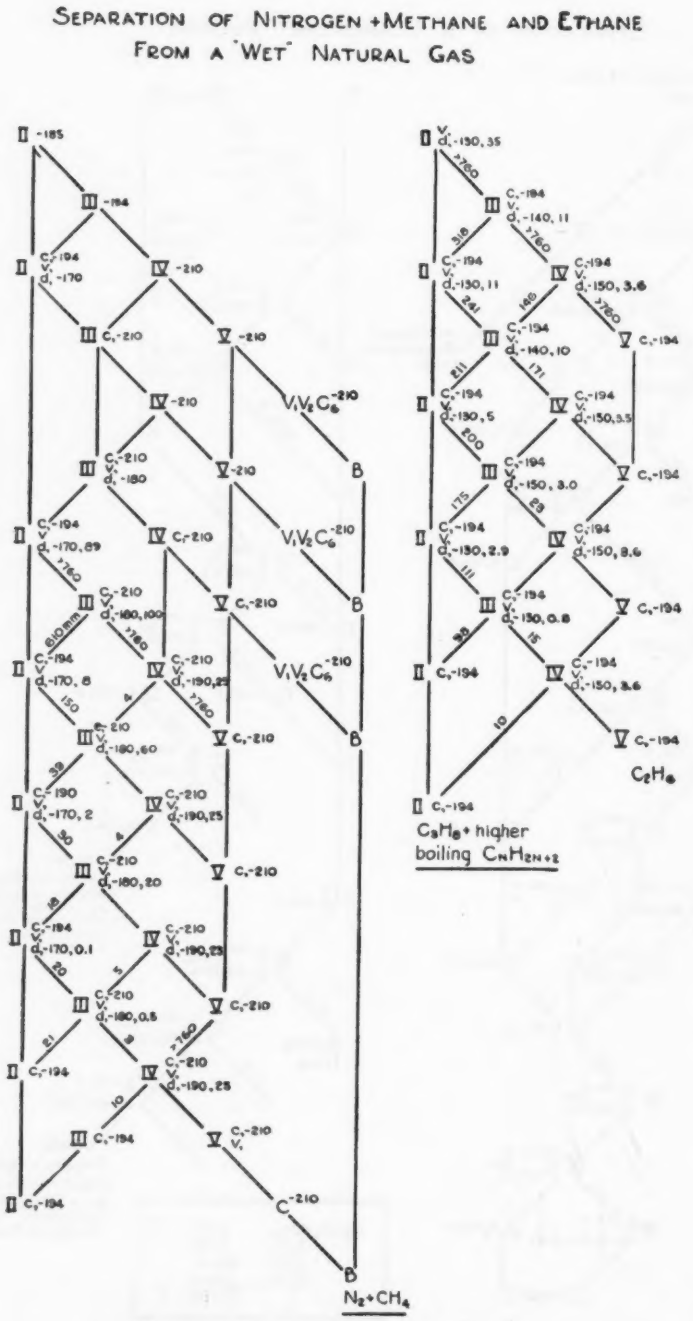


FIGURE 21.—*Fractionation chart No. 7*

the methane was pumped off from *II* with *III* and *IV* in series at −185° C. The distillation then proceeded normally from *II*.

The separation of ethane from the propane-plus residue required four cuts from the original mixture at −150° C. A better system would have included an initial cut at −130° to −140°, effecting the complete separation of ethane, if possible, followed by distillations at −150° to separate the ethane from the appreciable amount of propane carried over with the first distillate. Once the composition is known, it is usually possible to advantageously revise the system of fractionation, so that a check analysis requires less time.

The present chart illustrates how a separation is followed to completion. Having in mind the generalizations laid down in Section V, 5, the course of the separation is easily followed. The initial mixture possessed a vapor pressure of 2.5 mm at −150° C. The vapor pressure of the first distillate was raised to 3.5 at the same temperature, while that of the residue was lowered to 1.0. Similarly, the vapor pressure of the fourth residue in *I* had diminished to 0.04 mm, and the very small distillate from this residue possessed the same vapor pressure within 0.01 mm. Evidently the ethane had been completely removed from the residue in *I*. Traces of propane remained in the combined distillates in *III*, however, as was evidenced by the slight increase in vapor pressure (3.5 to 3.6) upon a further distillation. Only 10 mm of the residue remained from the further distillation of the distillate whose initial vapor pressure was 3.6 mm. When this was combined with the previous residue, the total pressure was 32 mm. The vapor pressure of this residue at −150° was 0.15 mm, well under the vapor pressure of ethane (3.6 mm), but over that of propane at the same temperature (approximately 0.05). A distillation of this residue recovered only 12 mm of distillate, the vapor pressure of which was 3.0 mm at −150°—clearly a mixture predominant in ethane but containing some propane. Since the gas volumes here involved were so small, the separation might well have been concluded forthwith. The final step was added simply to show how the residue could be worked back to a vapor pressure of 0.05 mm at −150°, from which a further distillation gave no measurable separation. The separations of propane and butane may be followed in a like manner. Since the partial pressures of butane and higher boiling components were low, the separation was carried out in the tubes *II* to *IV* rather than in the rectifying tube *I*. The propane was added to the ethane and lower boiling components and the natural gasoline determined from the butane and pentane-plus fractions.

Fractionation chart No. 2 (*fig. 16*).—In the case of this sample the natural gasoline content was desired without reference to the complete composition of the natural gas. Accordingly, the nitrogen,

methane, and ethane were separated in a double step, which also served to begin the separation of the propane fraction. The propane was first separated from the original mixture by a series of distillations at −130° C. It was soon evident that butane and higher boiling hydrocarbons were present in sufficient quantity to materially retard the complete separation of propane. The initial distilling temperature was therefore raised to −100° C., followed by second and third distillations at −130° C. The combined distillates from the series of third distillations were redistilled to safeguard against butane being carried into the final propane fraction. Thus, at the end of 23 distillations, propane was separated from the residue of higher boiling hydrocarbons and added to the ethane and lower boiling components.

There now remained in the residue a mixture of butane and higher boiling hydrocarbons, which subsequent analysis showed existed in the approximate ratio of $3C_4H_{10} : 2C_5H_{12}$ plus higher boiling components. This is an average condition which may be expected in many natural gas samples, and it is accordingly interesting to note the fact that the separation of the butane was not accomplished until the twenty-fifth distillation. At this point, however, propane was indicated in the butane fraction. Its presence would necessarily ruin the natural gasoline determination, and it was therefore separated from the butane by seven additional distillations. The butane fraction was then subjected to further separation to exclude possible traces of propane and isobutane which would interfere with the determination of natural gasoline. Three distillations divided the butane fraction into two roughly equal parts, and the higher boiling portion was retained for mixing with the pentane fraction in the ultimate determination of the gasoline.

Fractionation chart No. 3 (*fig. 17*).—The natural gas of chart No. 2 is evidently a type best separated with the aid of the rectifying tube. This is illustrated by chart No. 3.

Nitrogen, methane, and most of the ethane were removed exactly as before. The removal of propane from the higher boiling hydrocarbons, however, was accomplished by a single distillation in rectifying tube *I*, a temperature gradient of −100° to −130° C. being used for this purpose. The butane, carried over with the propane (and some ethane), was removed by a series of 11 distillations in the ordinary tubes *II* to *V*. The butane was then separated from the pentane by two separate distillations from the rectifying tube *I*, the temperature gradients of −60° to −90° C. and −70° to −100° C. being used. Twelve intermediate and additional distillations from tubes *II* to *V* served to return the pentane carried over with the butane.

Comparison of chart No. 2 with chart No. 3.—A comparison of the two methods used for separating this gas should now be made.

Nitrogen, methane, and the larger portion of the ethane were removed by the same procedure in both cases.

Propane was removed by 23 distillations from the plain tubes alone, while the initial use of the rectifying tube for one distillation made possible the completion of the separation with only 11 additional distillations from the plain tubes.

The initial distillation of propane from the plain tube did not result in the complete removal of ethane to the pump system, since the vapor pressure of the distillate remained as high as 12 mm at −130° C. for the second distillation. The vapor pressure of the corresponding distillate from the rectifying tube had dropped to 1.3 mm at the same temperature—about 0.3 mm above the vapor pressure of pure propane at that temperature.

A comparison of the vapor pressures of the distillates in both cases shows that the rectifying tube not only separated all of the propane from the higher boiling hydrocarbons but at the same time removed a distillate having a smaller boiling range. The vapor pressures of the distillates (in mm) in the case of the plain tubes were 12, 17; 3, 5, 15; 0.53, 0.77 1.8; 0.47, 0.74, 0.6, etc. The vapor pressures in the case of an initial distillation from the rectifying tube were 1.3, 4; 0.6, 0.9; 0.2, 0.7; 0.08, 0.09.

A similar comparison may be made for the butane separations. The plain tube method required 25 distillations to separate the butane from the pentane-plus residue and 7 additional distillations to remove some propane which had not been properly separated from the butane-plus residue. Two distillations from the rectifying tube yielded distillates containing all the butane and not nearly as much of the pentane, since only 12 additional distillations from the plain tubes were required to complete this fractionation.

Altogether, the first analysis required 45 distillations from the plain tubes, while the second required 3 from the rectifying tube and 23 from the plain tubes.

Limited use of the rectifying tube.—The question naturally suggests itself: Why not eliminate the plain tube altogether and carry out all distillations in a rectifying tube? Two considerations prevent such a method of attack. The first is less important but is, nevertheless, a real consideration. The total time required to establish proper temperature equilibrium and conduct the actual distillation thereafter is about four to five times greater when the rectifying tube is used. The case may then occur where no real saving of time is made by use of the rectifier. The main consideration, however, lies in the fact that the efficiency of the rectifying tube depends entirely on the amount of liquid refluxed from the top of the column. This means that the distillate must not only be withdrawn at a slower rate but also that there must be sufficient volume of liquid to reflux.

Toward the end of a separation the liquid volumes become very small, and the actual rectifying action of the column is almost negligible. It is therefore much better to use the plain tube during this part of the fractionation.

Unfortunately, in the case of a gas not previously examined it is not always apparent when the distillation should be changed from the rectifier to the plain tube. For example, referring to chart 3, the separation of propane might have been materially expedited by using the rectifying tube a second time instead of making the first distillation from *II* at −130° C., 1.3 mm. The cause of confusion here was that the vapor pressure of this particular distillate was almost that of pure propane and therefore indicated the presence of very little butane. Subsequent analysis developed the fact that the distillate was actually a mixture of ethane, propane, and butane. The ethane served to raise the vapor pressure just enough to lead to the false conclusion drawn.

The operator, however, is not apt to have the problem of continually examining natural gases from new fields. Rather, he will usually face the problem of analyzing gases of fairly well-known compositions, even when their sources are from various points of a plant cycle. He will then have the opportunity to determine upon the most advantageous method of separation by merely making a few preliminary separations of each type of gas of which the composition is to be determined.

In general, the rectifying tube should be used for "wet" natural gases and special samples, drawn from plant cycles, which contain large amounts of propane, butane, and the higher boiling hydrocarbons. The plain tube may be used for "dry" natural gases, outlet samples from natural gasoline extraction plants, and other mixtures containing small amounts of the heavier hydrocarbons. It should also be used for the final steps in the distillation of all types of gases.

Fractionation chart No. 4 (fig. 18).—This illustrates the separation of the outlet gas from the extraction plant which used the natural gas of charts 2 and 3 as a raw or inlet gas. It may be taken as fairly representative of the fractional separation of the "dry" type of gases. There are no points of especial interest, except to note that the propane separation was more difficult than had been anticipated, indicating the need of the rectifying tube. The butane separation, on the other hand, was quite easily carried out in the plain tubes. This condition is usually reversed for the case of an untreated "dry" natural gas, although the plain tubes are usually satisfactory for both the propane and butane separation.

Fractionation chart No. 5 (fig. 19).—This chart illustrates the separation of a typical "wet" gas and includes the determination of pro-

pane by itself as well as the usual three cuts made for the determination of natural gasoline. The rectifying tube was used. Two different temperature gradients were employed to remove ethane from the higher boiling hydrocarbons, and they should be particularly noted, since they are much higher than are ordinarily used. These gradients were chosen because of the unusually large proportion of the higher boiling components. The rectifier was again used for the propane and the butane separations. For this type of gas it would be desirable to have at least two rectifying tubes arranged in the order $I_a \rightarrow II \rightarrow I_b \rightarrow III \rightarrow IV \rightarrow V$. I_b and II should be connected so that they might be bypassed, permitting the independent connections $I_a \rightarrow II$, $I_a \rightarrow I_b$, $II \rightarrow I_b$ and $II \rightarrow III$. It would thus be possible to conduct two rectifications at once, using tubes II and III as condensers.

Fractionation chart No. 6 (fig. 20).—The separation of a commercial propane is illustrated by this chart. Ordinarily, a sample of approximately 1 liter would have been taken and the rectifying tube used. Preliminary information indicated the "propane" in question to be very nearly pure, and on this account a small volume was used and the plain tubes were employed. The sample contained only traces of methane and butane and a small percentage of ethane. The purities of the distillates were determined by the differential manometer method and the equations already mentioned.

Note on liquid samples.—It is quite possible to withdraw liquid samples from stills or other units of a "stablizing" or processing cycle and subject these to separation. Care should be taken to preserve the integrity of the liquid samples, since these have been found to fractionate during sampling. If the sample is withdrawn from a still under pressure, the valve admitting the sample to the receiver should be immersed in the still liquid itself and not placed outside the still shell at atmospheric temperature. The sample may be transferred to a small evacuated bulb of known volume and transferred directly to the evacuated distillation apparatus by condensation at liquid air temperatures. If the sample is entirely volatilized at room temperature, however, it is more convenient to sample and measure in the vapor phase.

The separation of liquid samples is best conducted by using the rectifying tube, as in chart 5, except that a greater number of ditillations should be made from these tubes and fewer from the plain tubes. The method has already found success in at least one commercial laboratory.

Fractionation chart No. 7 (fig. 21).—The proper interpretation of data obtained in the development of plant processes often requires a knowledge of the complete composition of a natural gas or special plant sample. While the entire separation is unnecessary for the determination of natural gasoline, it will be well to include a chart to

illustrate the separation of the nitrogen-methane and ethane fractions in order to supplement and complete the other charts here given. A "wet" natural gas was chosen as offering the most difficult type of separation which may be encountered. The separation of a "dry" natural gas will be merely a simplification of this case, involving fewer distillations.

Since the course of the distillation must be followed with reference to the vapor-pressure data, it is necessary to insure the complete removal of nitrogen, which does not condense at any of the temperatures here used or normally available but which is held strongly in solution by the methane. Most of the nitrogen was removed by initial distillations at $-185°\rightarrow -194°\rightarrow -210°$ with the pumps operating in series, and two following steps which include pumping for short periods during the second and third distillations, with condensing tubes held at $-210°$ interposed between the pumps and distilling tubes.

The subsequent separations were made by employing temperatures which were lowered 10° for each succeeding distillation, the initial temperatures selected being higher than desirable for a final separation but facilitating the removal of the more volatile component which is held in solution by relatively large amounts of the higher boiling fractions. Thus, the methane was separated by distillations at $-170°\rightarrow -180°\rightarrow -190°$ C., and the ethane separated at $-130°\rightarrow -140°\rightarrow -150°$ C.

It will be noted that a temperature of $-210°$ C. is necessary to reduce the vapor pressure of the methane fractions sufficiently to eliminate a measurable error which might result from methane left in the vapor phase above the residues of ethane and higher boiling components. This low temperature is obtained by reducing the pressure over the liquid air contained in the Dewar tubes surrounding the distilling tubes. Liquid air so cooled is apt to fracture a distilling tube if the latter is immersed directly from room temperature, since it apparently wets the glass immediately upon immersion, while liquid air boiling at atmospheric pressure does not. It is accordingly wise to precool the distilling tube with liquid air which is boiling at atmospheric pressure before immersing it in the liquid which has been cooled below its atmospheric boiling point.

VII. RECOMBINATION OF FRACTIONS FOR DETERMINATION OF NATURAL GASOLINE CONTENT

1. MEASUREMENT OF PENTANE FRACTION

The pentanes, together with heavier hydrocarbons, may be determined in the vapor phase simply by difference, or measured directly in the liquid phase. One method serves as a check on the other, and while the direct measurement is to be considered the more accurate

for purposes of computing natural gasoline per million cubic feet of gas, the vapor phase calculation has been found sufficiently accurate for most engineering needs and involves one less analytical operation.

If the liquid volume is determined, the special weight burette (fig. 3, B_1 of fig. 10) is used. The pentane-plus condensate will be in either of the distilling tubes *I* or *II* at the end of the fractional distillation. It is transferred to bulb *12* of the weight burette (see fig. 3) by vaporization and condensation at liquid air temperatures, stopcocks *31* and *32* being opened for this purpose.

The weight burette is described in detail in the reference previously cited.[20] For the operator's convenience the technique of operation may be outlined here. Reference is made to Figure 3.

The two bulbs *8* and *12* are accurately calibrated between etch marks *7* to *10* and *9* to *13*. The volume of *8* slightly exceeds that of *12*, which in turn represents a slight excess over the maximum volume to be determined. When measuring a condensate, these bulbs are immersed in water bath *16* resting on a movable platform. The lower outlets of the bulbs are brought up over the edge of the water bath and thence down to 2-way cock *14* and Y cock *15*. Mercury is supplied to the system from the auxiliary glass stoppered reservoir *4* and drained from the system through outlet *17*. The upper outlets of the bulbs terminate in 2-way cocks *2*, *3*, and *6*, which correspond to cocks *36*, *33*, and *32*, respectively, of the assembly diagram. (Fig. 10.)

The capillary leads interconnecting the bulbs and various stopcocks are of 0.5 mm bore. Larger bores tend to trap gas at the tops of the siphons. Furthermore, the adjustment of liquid menisci to etch marks in a tube of such small diameter results in a high accuracy.

Before making a volume measurement the capillary leads connecting reservoir *4* and bulbs *8* and *12* and drain tube *17* are filled with clean mercury introduced at *4*, care being taken to avoid trapping any air. Mercury is then adjusted to etch mark *13* by connecting *4* to *12* through cock *15*. Final accurate adjustment of the mercury column is obtained by turning cock *2* to the vacuum line and cracking needle valve *11* to admit just sufficient pressure to reservoir *4* to allow the mercury to creep slowly upward to the etch mark. The water bath is removed and liquid air brought around bulb *12* in order to transfer the condensate from tubes *I* or *II*. Stopcock *6* is then closed, the bulb allowed to rise to room temperature, whereupon the water bath is replaced. Mercury from *4* is now allowed to flow through cocks *14* and *15* to fill bulb *8* to etch mark *7*. This measured volume of mercury is then admitted from bulb *8* through *14* and *15* into bulb *12*. The flow from bulb *8* is stopped when the meniscus of the pentane

[20] See footnote 7, p. 1152.

condensate reaches etch mark *9* of bulb *12*. The mercury remaining in *8* is then drained through cock *14* and drain *17* into a weighed flask, the flow being arrested when the mercury meniscus reaches etch mark *10* of bulb *8*. The tip of drain *17* should be immersed in a dish of mercury just previous to this drainage and withdrawn just before the weighing flask is placed. The tip is then immersed in the outflowing mercury, and if etch mark *10* is overrun the mercury may be redrawn into the burette from the flask by applying vacuum through stopcock *3*. The mercury drained from *8* is weighed to 0.5 mg. The temperature of the water bath is observed.

The foregoing data are sufficient to calculate the volume of the pentane condensate (at the observed temperature) confined above the mercury in *12*:

(Volume of *8*) − (volume represented by weight of mercury remaining in *8* and drained therefrom for weighing) = (volume of mercury admitted to *12*).

(Volume of *12*) − (volume of mercury admitted to *12*) = (volume of condensate in *12*, which was desired).

The volume of the pentane condensate may then be corrected to 0° C. by applying the coefficient of expansion of pure pentane. Although the condensate is a mixture of pentane with the heavier hydrocarbons, this step introduces no appreciable error. In fact, the correction to 0° C. may in some cases be unnecessary and was actually not fully applied in the present work, since the volumes of pentane condensate obtaining from the original gas volumes used were so small that the correction was usually small. In the event volumes larger than 0.1 ml are obtained, the proper technique would be to conduct the measurements of liquid volumes at 0° C., thereby automatically eliminating the necessity for such corrections. This technique should always be applied in the case of gases containing large amounts of natural gasoline condensate and whenever the best accuracy obtainable is desired.

The method may appear roundabout at first glance, but it will be noted that it eliminates errors which might be caused by wetting of the walls of bulb *12* by the condensate and the consequent impossibility of confining this liquid completely above the mercury.

The burette is prepared for a second measurement by slowly withdrawing the mercury from *12*, care being taken that no pentane condensate creeps into the capillary below etch mark *13*. The condensate may be pumped off or vaporized and recondensed in the distillation train.

The burette is capable of measuring the volume of the condensate to within 0.001 ml, which represents an accuracy of well under 10 gallons of natural gasoline per million cubic feet of gas, if a gas sample as large as 1 liter is taken. Each 0.001 ml of condensate per

liter of sample corresponds to 7.480 gallons per million cubic feet. Consequently, when the liquid volume of a condensate is measured, it is recalculated according to the equation

$$G = \frac{N_1}{N_2}\ (7{,}480)$$

Where

G = gallons per million cubic feet,
N_1 = ml of condensate determined,
N_2 = liters of gas sample taken.

In order to conform with the practice of the industry, N_1 should be measured at 0° C. and N_2 at 60° F., 30 inches Hg. In the present work the reported values are for gas volumes measured at 0° C., 760 mm Hg, dry.

2. ADDITION OF BUTANE FRACTION

The butane fraction, which has been measured and stored in the burette B_2 (fig. 10), may now be subdivided roughly into several parts and recombined with the condensate of pentane and heavier hydrocarbons.

The first procedure in this final step of the analysis is the transference of the pentane fraction to the condensing bulb C_2 of the vapor pressure manometer M_6. C_2 is then surrounded with a water bath held at 100° F. (or any other fixed temperature that may be desired). The vapor pressure of the pentane fraction is then observed, care being taken to attain the proper equilibrium. (The volume of the vapor phase must be negligible in order that the maximum saturation pressure of the mixture be obtained. See previous discussion, Sec. V, 6, last paragraph.) Bulb C_2 is then again immersed in liquid air and connected to the burette through stopcocks *57*, *28*, *27*, *26*, and *24* in series. A portion (roughly one-tenth of the total volume) of the butane is thus transferred from the burette and combined with the pentane fraction. The volume of this transferred portion is measured by noting the loss in volume from the burette. The new condensate in C_2 is then surrounded with the 100° F. bath. After insuring equilibrium by vigorous stirring the increased vapor pressure is observed. If the operator so desires, this condensate may be transferred to the weight burette B_1 and its liquid volume measured. It is then recondensed in C_2, and a second measured portion of the butane remaining in burette B_2 is condensed into it, the increased vapor pressure of this second new mixture being observed at the same fixed temperature. In this manner data are obtained to show the change of vapor pressure (at the fixed temperature) dependent on the percentage of butane recombined with the original pentane fraction. A curve plotted from these data will reveal at a glance the maximum

amount of hydrocarbon condensate possessing any selected vapor pressure, over the range determined and at the temperature fixed, which it is possible to extract from the natural gas so examined. A number of such curves are given in the following section and their analytical significance discussed.

A possible modification of the method naturally suggests itself at this point. If a supply of pure normal butane were available, it would be necessary to make only one complete separation by the fractional distillation method previously described. The gas sample might simply be separated into butane plus lower boiling components and pentane plus higher boiling components. The auxiliary supply of pure butane could then be combined with the pentane fraction in exactly the same manner as described above. Since pure normal butane might be more easily prepared in a large plant rectifying column than by quantitative separation in a laboratory apparatus, the suggestion here given seems practicable. It is evident that such a method could not be used if the amount of butane in the original gas sample were insufficient to raise the vapor pressure of the pentane fraction to the required value. However, most natural gases contain more than enough butane for this purpose, and the method would be applicable in the majority of cases. Justification for its use could be predetermined in many cases where a number of related samples were to be tested.

VIII. ANALYTICAL RESULTS AND ACCURACY OBTAINABLE

1. VAPOR-PRESSURE CURVES OF MIXTURES OF PENTANE AND BUTANE FRACTIONS AND THEIR ANALYTICAL SIGNIFICANCE

In order to illustrate how the data obtained by measurements of the percentages in the vapor phase are recalculated to gallons of condensate per million cubic feet of gas, a number of typical curves are reproduced in Figure 22. These cases cover the range from a natural gas containing small percentages of pentane and heavier hydrocarbons to one containing large percentages of the higher boiling hydrocarbons. The fractionation charts of four of the gases studied have been given, and the curves are marked to correspond to the fractionation chart numbers. Thus, C_3 is the inlet gas of the extraction plant, the exit gas of which is C_4.

Referring to Figure 22, it will be noted that there are two curves for each gas. The curves marked with symbols which include the subscript $_V$ follow observed points. These points are indicated by open circles and represent the results of measurements in the vapor phase. The abscissas of these curves are expressed in terms of per cent by volume of condensable hydrocarbon vapor (pentane fraction plus butane) in the natural gas and are noted at the bottom of the sheet.

The curves marked by symbols which include the subscript L, the observed points of which are indicated by crossed circles, represent data obtained by measurements of the liquid phase. Their abscissas are expressed directly in gallons of condensate per million cubic feet of gas and are noted at the top of the sheet. The ordinates of both

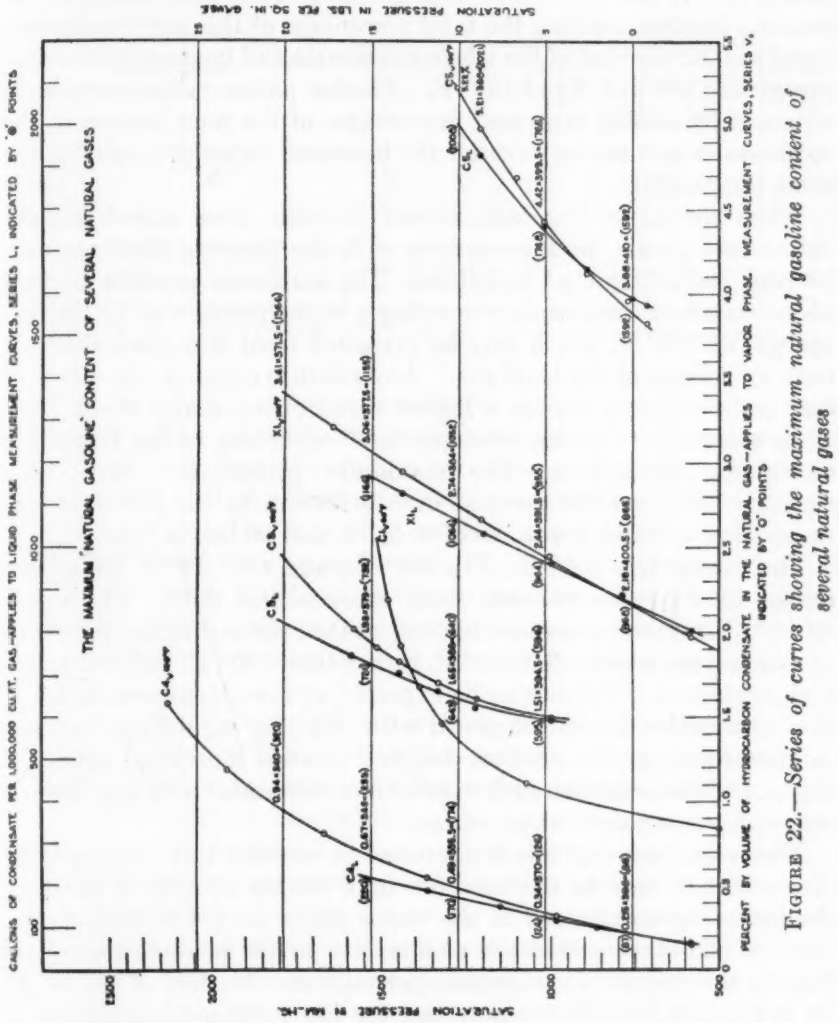

THE MAXIMUM NATURAL GASOLINE CONTENT OF SEVERAL NATURAL GASES
GALLONS OF CONDENSATE PER 1,000,000 CU.FT. GAS—APPLIES TO LIQUID PHASE MEASUREMENT CURVES, SERIES L, INDICATED BY "0" POINTS
PERCENT BY VOLUME OF HYDROCARBON CONDENSATE IN THE NATURAL GAS—APPLIES TO VAPOR PHASE MEASUREMENT CURVES, SERIES V, INDICATED BY "0" POINTS
SATURATION PRESSURE IN MM.-HG.
SATURATION PRESSURE IN LBS. PER SQ. IN. GAUGE

FIGURE 22.—*Series of curves showing the maximum natural gasoline content of several natural gases*

series of curves are expressed in saturation pressures, the scale at the left of the sheet being in mm of Hg and that at the right of the sheet in pounds per square inch gauge.

Consider, first, the series V, or vapor phase measurement curves, and take as an example the curve $C4_V$ (100° F.). The lowest point on this curve has an abscissa 0.15 and an ordinate 585.

This means that the pentane fraction which was separated from this gas consisted of 0.15 per cent by vapor volume of the total gas sample and possessed a vapor pressure of 585 mm Hg at 100° F. The second point of this curve has an abscissa 0.32 and an ordinate 985. This means that a portion of the pure butane fraction consisting of 0.17 per cent of the total gas sample has been added to the pentane fraction, making the total percentage of this new condensate equal to 0.32 per cent of the whole gas sample and increasing its vapor pressure to 985 mm Hg at 100° F. Further points on the curve were obtained by adding measured percentages of the pure butane to the condensates and noting in order the increased vapor pressures at the same temperature.

When the curve has been drawn through these experimentally determined points, its intersections with the pressure abscissas may be read and interpreted as follows: The maximum possible amount of hydrocarbon condensate possessing a vapor pressure of 10 lbs./in.^{2} (gauge) at 100° F. which may be extracted from this gas is 0.49 per cent by volume of the total gas. Any mixture occurring in excess of 0.49 per cent must possess a higher vapor pressure and would have to be shipped as "casing-head gasoline" according to the Interstate Commerce regulations. The maximum percentages have been similarly noted on the curve at intersections with the abscissas corresponding to vapor pressures of 0, 5, 15, and 20 lbs./in.^{2} gauge.

The curves $C3_V$ 100° F., $X1_V$ 100° F., and $C5_V$ 100° F have been drawn in the same manner from experimental data. The curve $C1_V$ 60° F. represents a series of condensates, the saturation pressures of which were measured at 60° F. rather than 100° F. and illustrates a characteristic difference to be expected at lower temperatures. If the investigator is not concerned with shipping regulations but has in mind some specific product designed to meet individual needs, he may, of course, examine such a series of condensates over any desired range of temperatures or pressures.

The natural-gas engineer is interested in knowing how many gallons of condensate may be obtained per unit volume of natural gas, and the percentages expressed in the vapor phase do not directly reveal this. If the exact percentage composition of the pentane fraction is known, the gallons of condensate per million cubic feet of gas might be calculated for this fraction and for the subsequent mixtures of this with the increments of pure butane. However, the separation of the pentane fraction is impractical in the present instance, not only because of the closeness of the boiling points of its components but also because of the fact that the amount of condensate available for fractionation is extremely small. While the separation is not impossible, it is not to be considered in the present work.

Another method of attack seems fairly simple. This follows from the consideration of the data tabulated below, which gives the volume relations of vapor and liquid phases for butane, pentane, hexane, and heptane.

TABLE 1.—*Volume relations of vapor and liquid phases*

Hydrocarbon	Density of liquid (0° C.) (I. C. T.)	Molecular weight	Weight of a normal liter of vapor (calculated)	Vapor volume which condenses to 1 volume of liquid	Cubic feet of vapor condensing to 1 gallon of liquid	Gallons per 10,000 cubic feet of vapor
Butane	0.601	58.08	2.591	232.0	31.02	322
Pentane	.64537	72.096	3.216	200.7	26.83	373
Hexane	.6769	86.112	3.842	176.2	23.56	425
Heptane	.70048	100.128	4.467	156.8	20.96	477

NOTE.—The vapor volumes in the foregoing table are all measured at 0° C., 760 mm Hg. The final column then expresses gallons of condensate at 0° C., per 10,000 cubic feet of dry vapor at 0° C., 760 mm Hg. If the natural-gas engineer desires to convert the butane factor to gallons (0° C.) per 10,000 cubic feet at 60° F., 30 inches Hg, the figure 305 should be used instead of 322 and should be applied as shown in the following discussion.

Since the gallons of condensate are usually reported per unit volume of 1,000,000 cubic feet of gas, the figures in the last column of this table represent the gallons of condensate which each hydrocarbon would yield if present to the extent of 1 per cent by volume in the total gas. In the light of these data it will be seen that appreciable error must result if an average factor is chosen to convert per cent by volume to gallons per million cubic feet. Such a conversion factor must depend not only on the actual initial composition of the pentane fraction but also upon the percentage of butane added at any step.

If, however, the actual liquid volume of the pentane fraction is measured by means of the weight burette (B_1), the calculation may be made to follow rather closely the change in percentage composition of the successive condensates. For example consider again the curve $C4_V$. The volume of the pentane fraction of this gas measured in the liquid phase was found to be 64.5 gallons per million cubic feet. This corresponded to 0.15 per cent by volume in the vapor phase. If this condensate had occurred to the extent of 1 per cent by volume of the total gas, the amount of condensate would have been 430 gallons per 1,000,000 cubic feet. For each 1 per cent by volume of butane existing as vapor in the total gas 322 gallons per 1,000,000 cubic feet might be condensed. If a line is now drawn with percentages of butane from 0 to 100 as abscissas and gallons per 1,000,000 cubic feet as ordinates, with the values 0 per cent butane = 430 gallons per 1,000,000 cubic feet and 100 per cent butane = 322 gallons per 1,000,000 cubic feet, the figures for gallons per 1,000,000 cubic feet corresponding to any percentage of butane in the mixture for each per cent of mixture present in the total gas may be read.

This has been done in Figure 23, of which the line *C4* refers to the sample under discussion. Referring back to curve $C4_V$ of Figure 22, the second experimental value noted is for a mixture representing 0.32 per cent of the total which was obtained by adding 0.17 per cent of butane to the 0.15 per cent of pentane-plus. The percentage of butane in this mixture is $0.17/0.32 = 42$. Reading from *C4* of Figure 23, the value corresponding to 42 per cent of butane is 385 gallons per million cubic feet; that is, for each 1 per cent by volume of the 42 per cent C_4H_{10} + 58 per cent C_5H_{12} + mixture present in the total gas, 385 gallons of condensate can be obtained from 1,000,000 cubic feet. Since there is 0.32 per cent of the mixture, it would yield $0.32 \times 385 = 100$ gallons per 1,000,000 cubic feet.

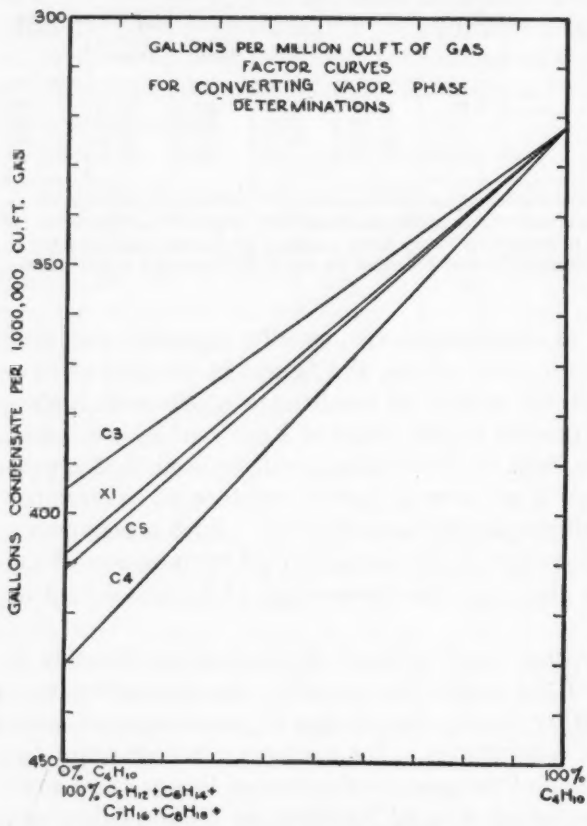


FIGURE 23.—*Factor curves for calculating vapor phase determinations*

These calculations have been noted for all the C_V curves of Figure 22 at points where they intersect the pressure ordinates of 0, 5, 10, 15, and 20 lbs./in.^{2} gauge. The notations have been made in the following order: Per cent condensate × conversion factor = gallons per million cubic feet. It may be noted in passing that the value of the saturation pressure for the pentane fraction of curve $C3_V$ indicates the presence of some butane in this residue.

The ultimate accuracy of this method will be limited by the precision of the separation by distillation. With a great deal of care a precision of 0.02 per cent of the total volume can be attained which (in the case of 1 liter of sample) would correspond to an accuracy of about 8 gallons per million cubic feet for the average condensate

having a vapor pressure of 10 lbs./in.^{2} Other sources of error are the incorrect measurement of gas volumes (negligible if a proper burette is used), failure to attain equilibrium in measuring vapor pressures (which may cause considerable errors), and the error in measurement of the liquid volume of the pentane condensate. The latter may result in an error of about the same magnitude as that arising from the limit of accuracy of the analytical separations.

2. COMPARISON OF MEASUREMENT OF NATURAL GASOLINE CONTENT AS DETERMINED IN VAPOR AND LIQUID PHASES

The natural gasoline content may be directly measured by means of the special weight burette. This method will eliminate some of the errors of the calculation from vapor phase measurements. The dependence upon the accuracy of the separation disappears, except that it is still absolutely essential that the butane fraction used shall contain no traces of propane or isobutane. The limiting accuracy lies in the measurement of the liquid volumes, and since this may be made to 0.001 ml the figure representing gallons per million cubic feet should be correct to within 7.48 if a liter sample of gas is taken. This direct measurement is accordingly to be recommended when best results are sought. The objection offered by the method is simply that a volume measurement requires care and a considerable amount of time, so that by comparison the procedure is both more complicated and time consuming.

A number of these direct determinations of the liquid volumes of the condensates were made. The experimental data are noted on the series C_L curves of Figure 22. The experimentally determined volumes were converted to gallons per million cubic feet. The plotted values are noted by the crossed circles. These curves form the basis for a direct comparison between the two methods of determining the natural gasoline content. The data are tabulated in Tables 2 and 3.

At the beginning of this work the Natural Gas Association Gasoline Committee named an accuracy of 10 gallons per million cubic feet as being entirely satisfactory for all purposes. A study of the data of Tables 2 and 3 shows that the calculation from vapor-phase data checks the direct measurement in the liquid phase within the limits required by the natural-gas engineer. The greatest difference noted between the two methods in the case of corresponding experimental values (Table 2) was 13 gallons per million cubic feet, and deviations from the average of the differences were all under 10 gallons per million cubic feet. In the case of values read from curves constructed from the experimental data (Table 3), the greatest difference noted was 17 gallons per million cubic feet, and the maximum deviation from the average of the differences was 10 gallons per million cubic feet. If all the values of Table 2 are considered, the average deviation

between the two methods becomes +1 gallon per million cubic feet. It seems safe to assume that the vapor-phase method, which is the shorter of the two, will satisfy the demands of all ordinary engineering calculations.

TABLE 2.—*Comparison of natural gasoline content obtained from direct measurement in liquid phase and calculated determination in vapor phase—Experimental values*

Gas	Liquid-phase method	Vapor-phase method	Deviation of vapor-phase calculation from liquid-phase measurement = Δ	Deviation from average Δ
	*Gallons per 1,000,000 ft.*³			
C4	65	65		
	99	100	+1	1
	116	119	+3	1
	152	148	−4	6
	187	194	+7	5
Average			+2	
C3	592	592		
	621	628	+7	6
	662	656	−6	7
	705	700	−5	6
	746	755	+9	8
Average			+1	
X1	804	804		
	886	884	−2	2
	963	958	−5	1
	1,034	1,029	−5	1
	1,128	1,119	−9	5
Average			−4	
C5	1,575	1,575		
	1,592	1,590	−2	9
	1,661	1,670	+9	7
	1,758	1,764	+6	1
	1,929	1,942	+13	6
Average			+7	

TABLE 3.—*Comparison of natural gasoline content obtained from liquid-phase and vapor-phase methods—Values read from C_V and C_L curves*

Gas	Vapor-pressure gauge	Liquid-phase method	Vapor-phase method	Δ	Deviation from average Δ
	*Lbs./in.*²	*Gallons per 1,000,000 ft.*³			
C4	0	87	86	−1	6
	5	124	126	+2	3
	10	170	174	+4	1
	15	220	233	+13	8
	20		320		
Average				+5	
C3	5	595	596	+1	1
	10	643	640	−3	5
	15	724	732	+8	6
Average				+2	
X1	0	868	865	−3	5
	5	964	955	−9	1
	10	1,064	1,052	−8	0
	15	1,166	1,155	−11	3
	20		1,266		
Average				−8	
C5	0	1,592	1,592	0	10
	5	1,748	1,765	+17	7
	10	2,008	2,021	+13	3
Average				+10	

3. COMPARISON OF RESULTS OBTAINED BY PRESENT METHODS WITH THOSE OBTAINED BY EXISTING FIELD AND LABORATORY METHODS

It now remains to compare the analytical results obtained by the methods here described with those obtained by various existing field and laboratory methods. The latter comprise the oil absorption and charcoal adsorption methods in various modifications. Results reported for these field methods were obtained by members of the Gasoline Committee of the Natural Gas Association in connection with their standardization work.

The comparative data are assembled in Table 4. The first two columns of this table give the results of the methods here developed. The following columns give the reported results of the other methods for the same gases, together with their actual and percentage deviations from the new methods taken as standards. The figures reported for these tests are, in general, averages of an unreported number of tests. Check values reported for the same method are noted by braces. Otherwise, when more than one value is reported, the gas has been tested by several modifications of the same general method.

Only three cases occur in which the ordinary methods gave higher results than the new method. In all three cases the determination was made by the method of charcoal adsorption. Two of these three determinations yielded satisfactory checks with the proposed standard method; the third, which was 21.2 per cent high, is explained by the fact that the vapor pressure of the condensate obtained from the charcoal exceeded 10 lbs./in.^{2}.

The closest checks observed between the ordinary and new methods were -2.0 and $+2.2$ per cent. The greatest discrepancies were approximately -55 per cent. The average deviation was approximately -26 per cent for the case of oil absorption and -23 per cent for the case of charcoal adsorption. (In obtaining these figures the braced values of Table 4 were not taken independently but averaged, and each set weighted as a single determination.) If the values for the gas X6 are excepted, the range of percentage deviation from the reference method is -2.0 to -42.2 per cent for oil-absorption tests and $+21.2$ to -44.5 per cent for charcoal-adsorption tests. There is apparently little justification for preferring one of these methods to the other when both are judged on the basis of these results.

There are three general conclusions to be drawn from the comparative data. The first is that different modifications of the same field-laboratory method yield results which do not always agree. The second is that no modification of the oil absorption method gives results which agree with any modification of the charcoal adsorption method. The third is that both the oil absorption and charcoal adsorption methods give results which are too low.

TABLE 4.—*Comparison of results obtained by methods described with those obtained by existing field and laboratory methods*

Natural gas sample	"Natural gasoline" content expressed in gallons per million cubic feet							
	From the direct measurement in the liquid phase Vapor pressure 10 pounds per square inch (gauge) at 100° F. (1)	From calculations of vapor phase determinations. Vapor pressure 10 pounds per square inch (guage) at 100° F. (2)	Reported from oil absorption methods [1]	Deviation from methods (1) and (2) oil absorption	Percentage difference from methods (1) and (2)	Reported from charcoal adsorption methods [1]	Deviation from methods (1) and (2)	Percentage difference from methods (1) and (2)
C3. Pennsylvania, untreated	643	640				497	(1) −146	−22.7
C4. Pennsylvania, treated	170	174				182	(1) +12	+7.1
C5. Wyoming, untreated	2,008	2,021				1,300	(1) −708	−35.3
						1,380	−628	−31.3
						1,600	−408	−20.3
						1,450	−558	−27.8
						1,570	−438	−21.8
						1,620	−388	−19.3
X1. Pennsylvania, untreated	1,064	1,052	944	(1) −120	−11.3	1,290	(1) +226	+21.2
			1,043	−21	−2.0			
X2. Pennsylvania, untreated		270	210	(2) −60	−22.2	276	(2) +6	+2.2
			193	−77	−28.5			
X3. Pennsylvania, untreated		644	465	(2) −179	−38.5	564	(2) −80	−12.4
			453	−191	−42.2			
X4. Pennsylvania, untreated		6,520	5,839	(2) −681	−10.3	6,448	(2) −72	−1.1
X5. Ohio, untreated		806				654	(2) −152	−18.9
						469	−337	−41.8
						154	(2) −152	−49.7
						135	−171	−55.4
						120	−186	−60.8
X6. Oklahoma		306	148	(2) −158	−52.1	166	−140	−45.8
						138	−168	−55.0
						135	−171	−55.9
						158	−148	−48.4
						162	−144	−47.1
						133	−173	−56.6
X7. Texas, treated		380				211	(2) −169	−44.5

[1] Figures are given for several modifications of the same method where available. Braced figures indicate check analyses obtained by identical procedure. Other figures are, in general, averages from an unreported number of determinations. The figures in parentheses indicate the method used.

All of these facts were to be expected, since the oil absorption and charcoal adsorption methods involve many variable factors, some of which are not readily controlled. Even a thorough standardization of these test methods can not entirely eliminate some of these variable factors, and back of these considerations lies this fundamental difficulty—the ordinary sorption methods seek to determine a substance which has no identity. The substance isolated by the test is called the thing sought. If this were entirely reproducible, the idea would be convenient. Since it is not, confusion must result. The results obtained by the new method can not be strictly compared with those yielded by the ordinary methods, since the new method isolates a perfectly definite condensate which can be analytically reproduced

IX. CONCLUSION

It has been shown that an exact definition of the term "natural gasoline" is a prerequisite to the determination of the actual natural gasoline content of a natural gas. A definition has been developed which describes the maximum amount of condensate, complying with shipping regulations, that can be extracted from a natural gas. A method has been developed for the accurate determination of natural gasoline thus defined. Analyses made by this proposed standard method have been compared with those made by the ordinary existing methods. The data obtained indicate that the natural gasoline content of a natural gas can only be determined by the use of such a method as the proposed standard one, since existing field and laboratory methods yield results which do not agree among themselves and, in general, are lower than values obtained by the standard method. It is further evident that the interpretation of experimental plant data, the determination of actual plant efficiencies, the study of the action of rectifying columns for the removal of propane from natural gasoline or for the production of special fractions from the natural gas condensates, and other special investigational problems must depend for their true solution upon such a reference method as here developed.

WASHINGTON, October 10, 1928.

RELATION OF RADIO WAVE PROPAGATION TO DISTURBANCES IN TERRESTRIAL MAGNETISM

By Ivy Jane Wymore

ABSTRACT

This paper presents the results of a study of an apparent interrelationship between radio reception and changes in the earth's magnetism. The results show that for long-wave daylight reception over great distances (4,000 to 7,100 km) there is, in general, a variable but definite increase in the intensity of the received signal following the height of severe magnetic disturbance. This increase reaches its maximum in from one to two days and disappears in from four to five days. For moderate distances (250 to 459 km) there is an increase in the intensity of the received signal noticeable before as well as after the magnetic storm reaches a maximum. These changes in intensity cover periods from two to four days both before and after the magnetic storm reaches its height.

In a paper presented before the Institute of Radio Engineers in May, 1925, Espenschied, Anderson, and Bailey [1] pointed out that at times of severe magnetic storms abnormal radio transmission was likely to occur, night field intensities being greatly reduced and daylight intensities slightly increased. These conclusions were based upon hourly observations (for one day a week) of low-frequency transmission (57 kc) across the Atlantic covering a period of about two years. From a more exhaustive analysis of this same material, with the addition of later observations, Anderson [2] in 1928 concludes:

> High daylight radio field strengths (at 57 kc) obtain during periods of marked magnetic activity. In most cases the magnetic disturbances precede the high values, but there is evidence of an abrupt rise to high values preceding the magnetic disturbance and at times a gradual rise to high values independent of the magnetic activity. * * * It is seen that the high radio fields do not occur particularly on days of high magnetic character but rather during periods when magnetic storms occur. Because the radio data are available for one day a week only, no detailed conclusions can be drawn. For the most part, however, the high fields follow the magnetic disturbance and then gradually fall off.

Pickard,[3] from a series of observations on broadcast reception taken at Newton Center, Mass., on the Chicago station WBBM (800 to 900 kc), concludes that the "depression of night reception accompanying magnetic storms is very striking. Day reception from Nauen, AGS (24 kc), shows an inverse effect, and increase of field accompanying and following the storm."

[1] Espenschied, Anderson, and Bailey, Bell Tech. J., **13,** No. 3; 1925; Proc. I. R. E., **14,** p. 7; 1926.
[2] C. N. Anderson, Proc. I. R. E., **16,** No. 3, p. 297; 1928.
[3] G. W. Pickard, Proc. I. R. E., **15,** No. 2, p. 83; 1927; No. 9, p. 749; 1927; No. 12, p. 1004; 1927.

In a paper [4] presented before a meeting of the International Union of Scientific Radio Telegraphy in Washington, October, 1927, it was pointed out that the field intensity of the American station WSS (18.5 kc) for the duration of eight months when averaged in periods of five days, exhibited a marked tendency to vary with the diurnal range of horizontal intensity of the earth's magnetic field. This indicated the possibility of a day by day relationship between magnetic disturbances and variations in signal strength. The present study was, therefore, undertaken to determine whether such a correlation existed. A long series of reception data consisting of daily observations on low-frequency stations (15 to 23.4 kc) was available, which was particularly suitable for this investigation. These measurements had been made at the Bureau of Standards by the telephone-current comparator method.[5] Field intensity measurements from two groups of stations were examined—those made on signals from long distances (4,000 to 7,100 km) and those on signals from moderate distances (less than 500 km). For the former observations taken from 10 to 11 a. m. on Lafayette (LY), Ste. Assise (FU and FT), Nauen (AGS and AGW), Rugby (GBR), Coltano (ICC), and Bolinas (KET) were utilized, and for the latter observations at 10 a. m. and 3 p. m. on the Radio Corporation stations at Tuckerton, N. J. (WGG); New Brunswick, N. J. (WRT and WII); and Rocky Point, L. I. (WSS). In order to eliminate as much as possible any variations due to conditions not generally effective, stations of approximately the same wave length were grouped and the data were averaged. Thus, in Figure 1, LY (15.9 kc), FU (15.0 kc), AGW (16.5 kc), and GBR (16.1 kc) are grouped together; in Figure 3, AGS (23.4 kc), FT (20.8 kc), Bolinas KET (22.9 kc), and ICC (19.9 kc); and in Figure 4, the Radio Corporation stations WII (21.8 kc), WGG (18.9 kc), WRT (22.7 kc), and WSS (18.7 kc).

The field intensity of low-frequency signals is believed to be less influenced by magnetic storms than that of the broadcast range. For this reason only the most severe disturbances were considered in the calculations. Since practically all severe magnetic storms occur simultaneously over the earth, the observations taken at the Cheltenham Magnetic Observatory, of the United States Coast and Geodetic Survey, were considered sufficiently indicative of changes in magnetic activity. As a qualitative measure of daily magnetic activity, "magnetic character of day" numbers [6] were used to determine the occurrence of and to locate the central day of the magnetic storms which were selected in preparing the data in Figures 1, 3, and 4, and the

[4] L. W. Austin and I. J. Wymore, Proc. I. R. E., **16**, No. 2, p. 166; 1928.

[5] L. W. Austin and E. B. Judson, Proc. I. R. E., **12**, p. 521; 1924.

[6] For a qualitative estimate of magnetic conditions days are commonly divided into three classes and designated as follows: 0 denotes days which are magnetically quiet; 1, moderately disturbed days; and 2, severely disturbed days.

diurnal range of horizontal intensity of the earth's magnetic field was used for comparison in Figures 5 and 6.

Days for which the magnetic character number was reported as 2 at Cheltenham, Md., were considered days of maximum magnetic activity and are represented by the zero point of the abscissae in Figures 1, 3, and 4; that is, they are the central days of 11-day periods extending from five days before to five days after each magnetic storm. Averages were made of the radio field intensity of the stations on the corresponding days of these 11-day periods

The following table gives the dates of the magnetic storms considered in the calculations:

1925	1926	1927
Jan. 19-20.	Jan. 26-27.	Mar. 28.
May 4.	Feb. 23-24.	Apr. 14.
June 13.	Mar. 5.	May 5.
June 24.	Apr. 14-16.	July 21-22.
July 26.	May 4-5.	Aug. 20-21.
Aug. 22-23.	June 1-2.	Oct. 10.
Sept. 1-2.	Sept. 9.	Oct. 12.
Sept. 14-15.	Sept. 15.	Oct. 22-23.
Sept. 21.	Sept. 20-21.	
Oct. 23-24.	Oct. 14-16.	
Nov. 9.		

In Figure 1 are given the daylight values of the percentage deviations from the corresponding monthly averages of signal intensity of the long-wave European stations (LY, FU, AGW, and GBR) during the time of greatly increased activity of the sun in the years 1925, 1926, and 1927. While the values for the curves are smoothed, they approximate closely the actual deviations obtained. The trend of the curves before the maximum of the magnetic storms varies somewhat in the three years although, in general, it tends to fall below the average. The most striking similarity is the high value on all the curves on the second day after the peaks of the storms. In connection with this, the behavior of signals at the time of one extremely severe disturbance, that of October 12, 1927, is interesting. In Figure 2 the percentage deviations from the monthly averages of field intensity for the stations, Lafayette (LY), Nauen (AGS), and Bolinas (KET) at the time of this storm are given. Intensities well above average were observed on October 12, the day of the maximum disturbance, but on October 14, two days following, the intensity had increased so greatly that in some cases it was more than 200 per cent above the average value for the month. This increase in signal strength is too great to be a recovery from an abnormal condition before the storm and so probably represents some real effect of the condition productive of the magnetic disturbance.

In order to obtain some idea of the variation of signal strength on magnetically quiet days, an average for each of three years was made

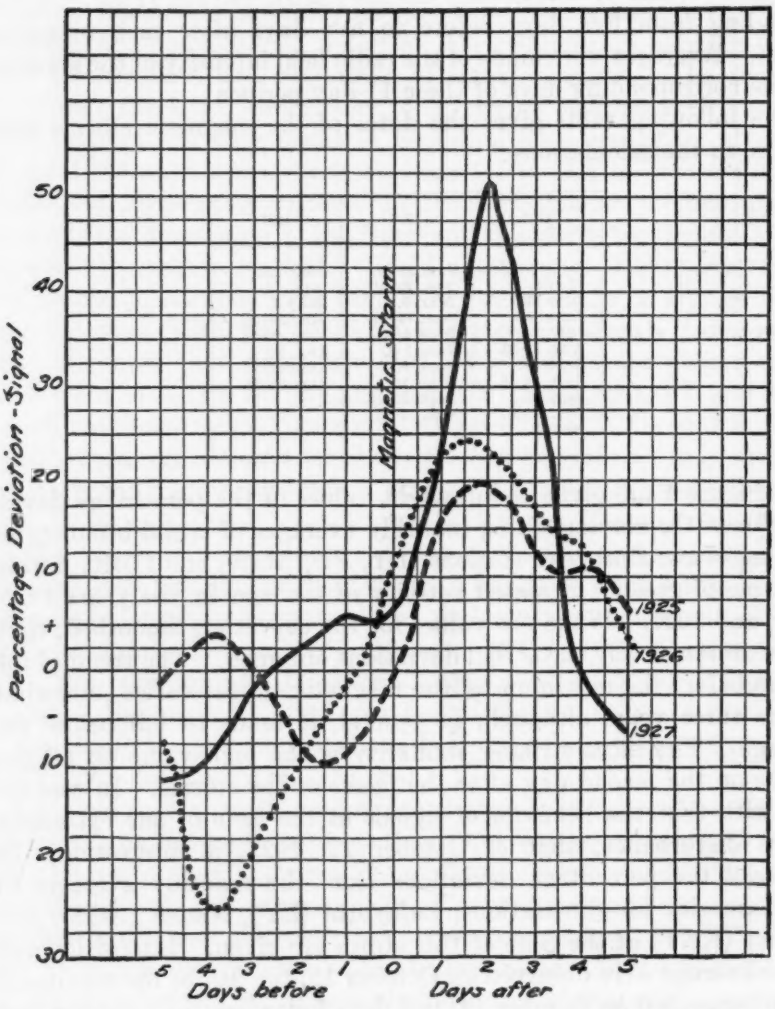


FIGURE 1.—*Average daily deviation from the monthly mean of daylight field strength of signal from stations in Europe (LY, FU, AGW, GBR) during the progress of magnetic storms, 1925, 1926, 1927*

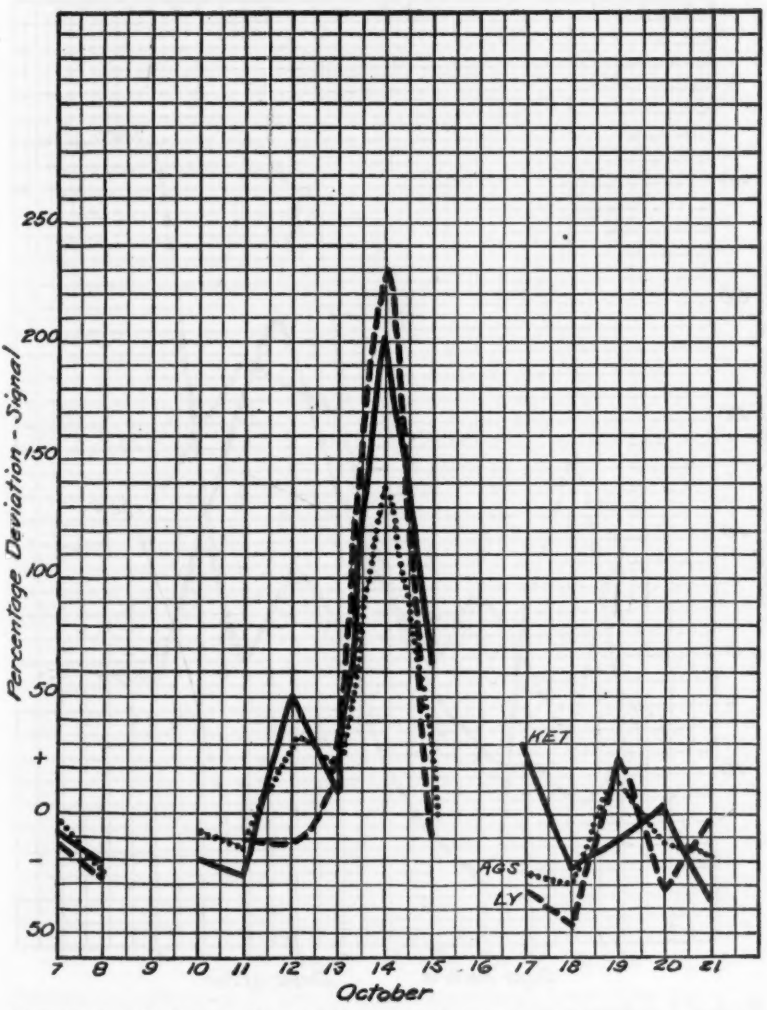


FIGURE 2.—*Deviations in signal strength from the monthly average during the progress of the magnetic storm of October 12, 1927*

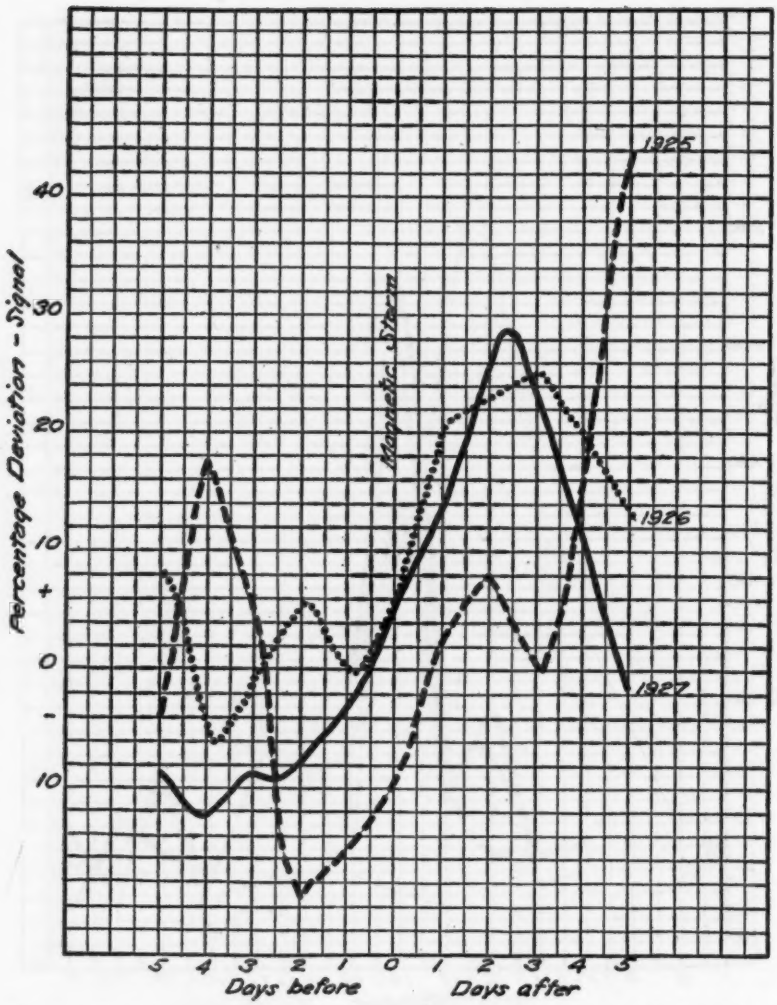


FIGURE 3.—*Average daily deviation from the monthly mean of daylight field strength of signal from stations in Europe and California (FT, AGS, KET, ICC) during the progress of magnetic storms, 1925, 1926, 1927*

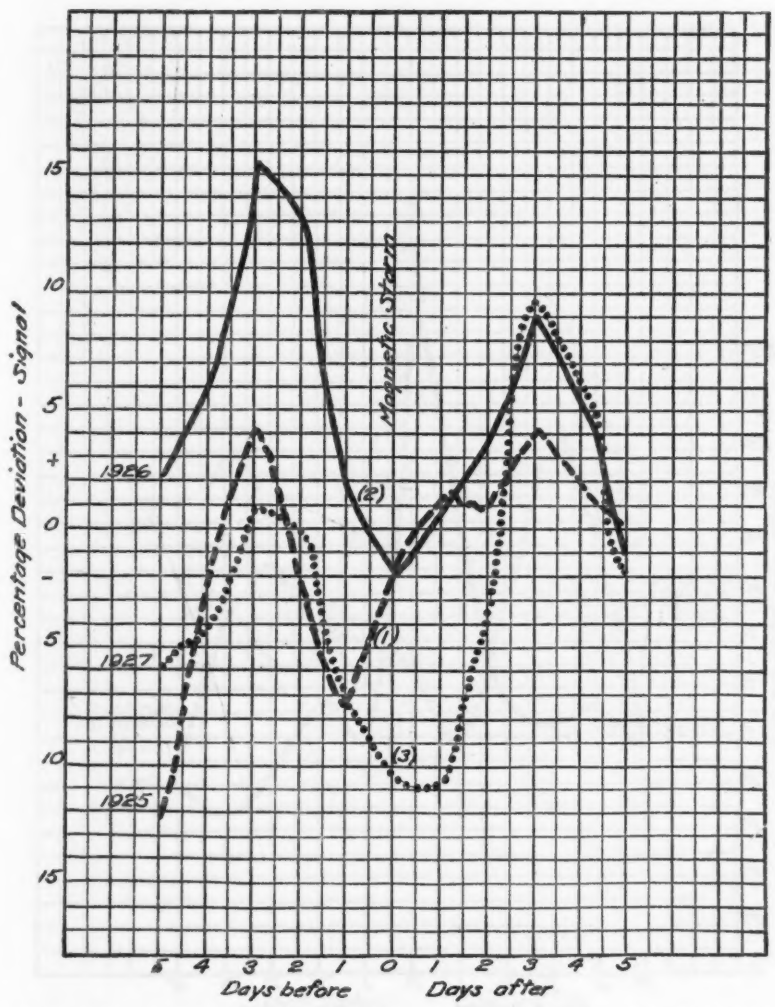


FIGURE 4.—*Average daily deviation from the monthly mean of daylight field strength of signal from stations in New Jersey and Long Island during the progress of magnetic storms, 1927*

(1) WII and WGG, 1925; (2) WII, WGG, and WSS, 1926; (3) WII, WGG, WSS, and WRT

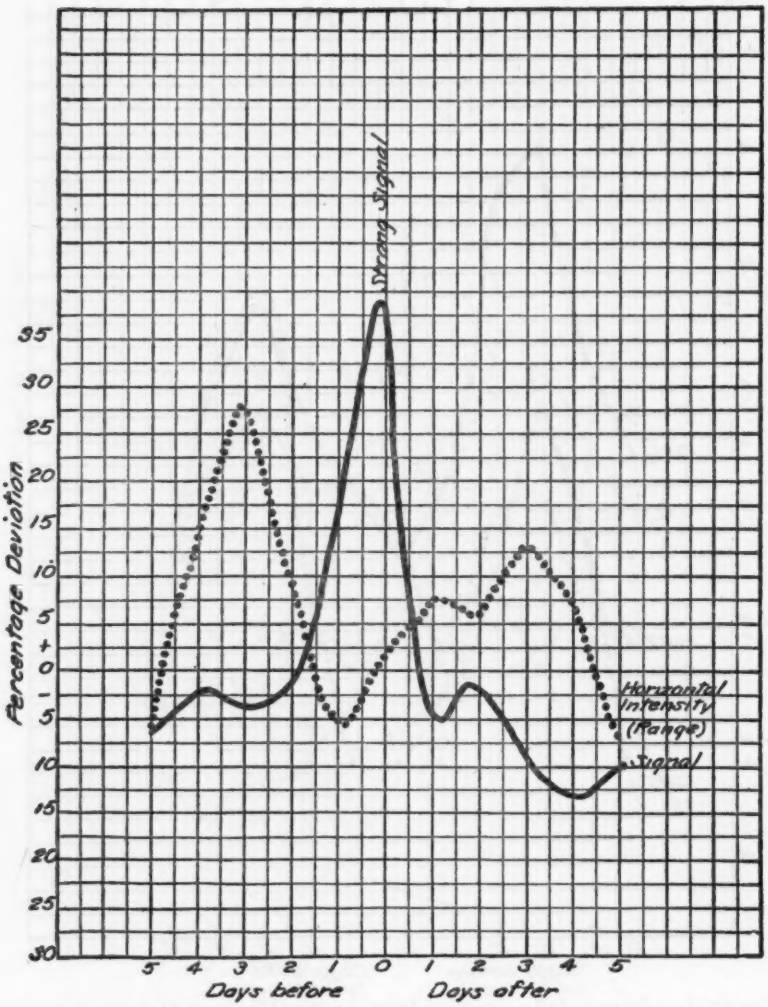


FIGURE 5.—*Average daily deviation from the monthly mean of daylight field strength of signal (Rocky Point, WSS) and of horizontal intensity (range) of the earth's magnetic field, 1926*

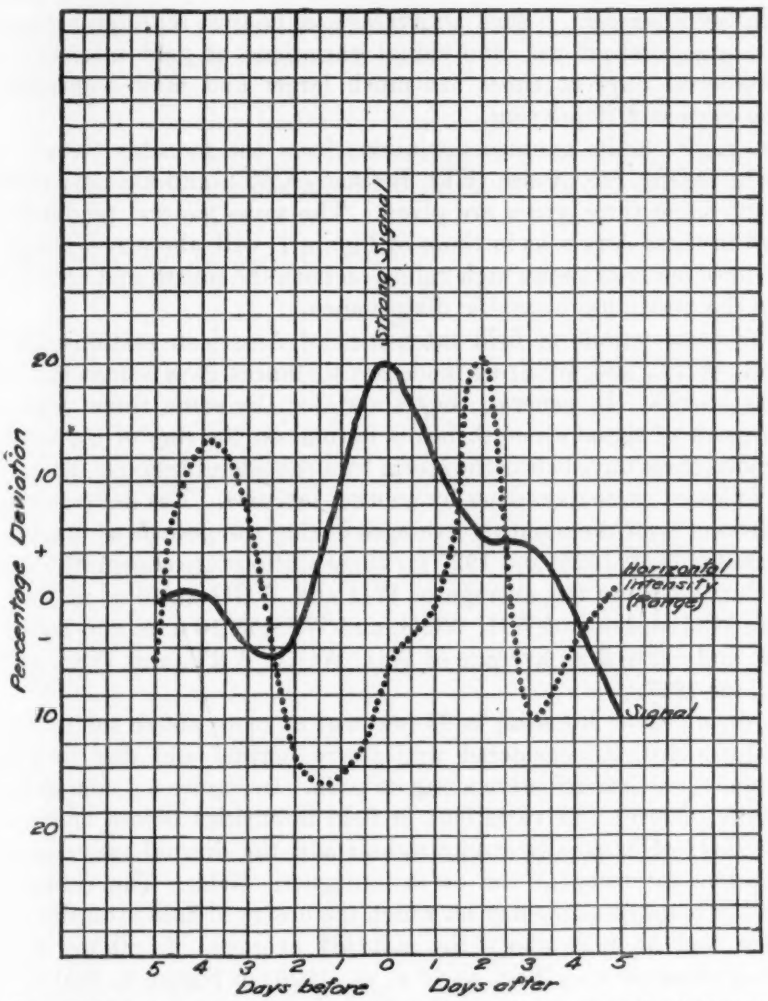


FIGURE 6.—*Average daily deviation from the monthly mean of daylight field strength of signal (New Brunswick, WII) and of horizontal intensity (range) of the earth's magnetic field, January to July, 1927*

for 12 days which were reported as magnetically quiet (magnetic character number = 0) and which were removed by five or more days from any reported disturbance. For 1925 these results gave an average signal deviation from the monthly average of two-tenths of 1 per cent for quiet days; for 1926, six-tenths of 1 per cent; and for 1927 one-tenth of 1 per cent, the mean for the three years being three-tenths of 1 per cent. Such an average, of course, represents merely the normal variations. Individual variations of field intensity on undisturbed days at times are much larger and may occasionally reach or exceed 10 per cent.

In Figure 3 the average deviations from the monthly means for Nauen (AGS), Ste. Assise (FT), Bolinas (KET), and Coltano (ICC) for the same three years are given. The same general tendency is noted in these curves as in those of Figure 1, with the exception that the curve for 1925 shows high values on both the fourth and fifth days after the maximum magnetic disturbance.

The observations of field intensities of American stations (WII, WGG, WRT, and WSS) at moderate distances gave somewhat different results. In general, they show, for the same three years, a depression of signal strength below normal on the day of the storm, preceded three days before the storm by a considerable rise in intensity and followed three days after by another increase. The daily average deviations from the monthly averages during the periods of magnetic storms for 1925, 1926, and 1927 for these stations are shown in Figure 4. Curve *1* gives the average of WII and WGG at 10 a. m. and 3 p. m., 1925; curve *2* of WII, WGG, and WSS, at 10 a. m and 3 p. m., 1926; and curve *3* an average of WII, WGG, WRT, and WSS, at 10 a. m. for 1927.

A signal whose intensity is 25 per cent or more above the average for the month is considered well above normal and due to some unusual conditions effective along its path. In Figure 5 a comparison is made between the variations in field intensities before and after these days of unusually strong signals and the diurnal range of the horizontal intensity of the earth's magnetic field. The center or zero day is taken as the day on which the observed field intensity was 25 per cent or more above the monthly average. In Figure 5 the station observed was WSS, at 10 a. m., 1926; in Figure 6, WII at 10 a. m., 1927. High values of the diurnal range occurred three days before and from two to three days after the signal peak. All data were smoothed by the formula

$$\frac{a+2b+c}{4}$$

From the foregoing curves it is evident that during periods of magnetic storms the behavior of low-frequency (15 to 24 kc) daylight signals tends to be as follows:

1. *Over long distances (4,000 to 7,100 km).*—The intensity of signal falls below normal for several days before the maximum magnetic disturbance, which is followed by a definite increase in strength from one to four days after the storm.

2. *Over moderate distances (250 to 400 km).*—There is an increase in signal strength above the average from two to four days before the disturbance with values below normal during the height of the storm followed by a strong increase in intensity from two to four days after the storm.

This work was done under the direction of Dr. L. W. Austin at the laboratory for special radio transmission research, Bureau of Standards. The observations were made by E. B. Judson at that laboratory.

WASHINGTON, January 12, 1929.

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